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Review article

Recent advances in the application of biochar in microbial electrochemical cells

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ABSTRACT

The International Biochar Initiative classifies biochar as "a solid material derived from the carbonization of biomass." Biochar is a solid substance produced during the thermochemical degradation of biomass. This paper describes several examinations that have been conducted to investigate novel utilization of biomass since biochar is affordable, environmentally beneficial, and can be utilized for diverse purposes, such as soil stabilization, wastewater treatment, greenhouse gas management and power generation. Biochar has also been applied in fuel cells and supercapacitors, according to the latest reports. Biochar has the potential to be new and tenable material for microbial fuel cell electrodes. Biochar MFCs made through pyrolysis and gasification, exhibited significant performance as compared to activated carbon and graphite granule. This paper emphasizes the use of biochar as electrodes in MFCs to facilitate the simultaneous treatment of wastewater and electricity generation while also providing additional commercial advantages. Applications of biochar in microbial fuel cells as

Abbreviations: 3D-EMFC, 3-Dimensional Electrode MFC; AMBC, American Bancorp of Ohio; AO, Acid Orange; ASTM, The American Society for Testing and Materials; BCw, Wood-based Biomass; BET, Brunauer–Emmett–Teller; CCS, Carbon Capture and Storage; CNCB, Carbon Nanoparticle-Coated Porous Biochar; COD, Chemical Oxygen Demand; CS, Carbon Sheets; CV, Cyclic Voltammetry; DIN, Deutsche Institut fur Normung; EAB, Electro-Active Bacteria; EDLCS, Electrical Double-Layer Capacitors; EDX, Energy Dispersive X-ray; EIS EPGC-800-2, Electrical Impedance Spectroscopy Eggplant-derived Graphitic Carbon-800-2; FARO, Federal Agricultural Research Oryza; FTIR, Fourier Transform Infrared Spectroscopy; GP, Graphite Particle; GS-15, General Schedule-15; HTC, Hydrothermal Torrefaction or Carbonization; ICP-AES, Inductively Coupled Plasma - Atomic Emission Spectrometry; ISO, International Organization for Standardization; LCCA, Life Cycle Cost Analysis; LED, Light-Emitting Diode; M, Molar; MESs, Microbial Electrochemical Systems; MFC, Microbial Fuel Cell; NMR, Nuclear Magnetic Resonance; OMW, Olive Mill Waste; ORR, Oxygen Reduction Reaction; PANI, Pseudo-Automatic Number Identification; PBS, Phosphate-Buffered Saline; PEDOT, Poly (3,4-ethylene dioxythiophene) polystyrene sulfonate; PEM, Proton Exchange Membrane; PMFC-RBC, PMFCs with Rice Plants and Biochar Anodes; PMFC-RCF, PMFCs with Rice Plants and Carbon Felt Anodes; PMFCS, Plant Microbial Fuel Cells; PTFE, Polytetrafluoroethylene; PVA, Polyvinyl Alcohol; RDE, Real Driving Emissions; SCS, Stabilization and Control System; SEM, Scanning Electron Microscope; SFG, Surface Functional Group; SM-10, Carbon-monolith 10; SMFC, Soil Microbial Fuel Cells; SMZ, Sulfamethoxazole; TEM, Transmission Electron Microscopy; TPD, Temperature-Programmed Desorption; UPS, Uninterruptible Power Supply; V, Voltage; VC, Vulcan Carbon; WDB, Workforce Development Board; XPS, X-ray Photoelectron Spectroscopy; XRD, X-Ray Diffraction; XRF, X-ray Fluorescence Spectroscopy; Z0, Initial Impedance; Z00, Negative Hypothetical Impedance.

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separator membrane and cathode catalysts are also mentioned. Brief information on the future prospects of the use of biochar in microbial fuel cells is further summarized.

1. Introduction

Since the green revolution, industrial development and greater adoption of agrochemical-based agricultural cultivation practices have substantially enhanced chronic organic and heavy metal pollution in the food web and atmosphere. This has sparked massive social anxiety about environmental conservation and community health. Precipitation, ion exchange, adsorption (via carbon activation), and membrane segregation procedures are some of the traditional techniques for extracting persistent contaminants from aqueous and gaseous phases [1]. These procedures are expensive and they frequently produce a large number of chemical leftovers that have little commercial use.

Microbial fuel cell (MFC) is a latest innovative technology that can accomplish organic and inorganic biodegradation while generating power. However, the expensive and non-renewable nature of current electrode materials is a major hurdle to the adoption of larger-scale MFC systems. Biomass-derived black carbon (biochar) could be a potential option for generating cost-effective and ecologically friendly electrode materials for MFCs. Biochar is a porous carbonaceous substance created when feedstocks such as wood chips or biodegradable wastes are thermochemically decomposed in the absence of oxygen. Pyrolysis, hydrothermal carbonization, microwave warming gasification and torrefaction are examples of thermochemical decomposition methods that differ in thermochemical temperature and period [2]. Biochar has sparked a lot of attention because of its advantages including an abundance of an active functional group on the surface and limited emission of greenhouse gases [3,4]. Biochar can be used in the treatment of wastewater, soil remediation, gas storage and segregation. Numerous Experiments are being conducted on the improvement of biochar generation and applications, with a special emphasis on biochar's potential in wastewater treatment. Toxic metals, organic contaminants, and nutrients have all been removed from wastewater using biochar as an adsorbent. Therefore, biochar is becoming more popular as a solution to current issues like changes in the climate, contamination, and soil degradation [3].

Biochar is a porous substance with negative surface functional groups that are made from a variety of source ingredients. In most cases, pure biochar in microbial fuels cells has a lower adsorption capability to pollutants in an aqueous medium, particularly highly concentrated effluent, than activated biochar. Furthermore, the use of virgin biochar is challenging in wastewater treatment owing to its low density and minute particle size, which severely restricts its application on large scale. Various techniques have been established and employed in sewage management and soil remediation, also in energy storage, to enhance the adsorption potential of biochar in microbial fuel cells and its employment in various sectors. Biochar engineering is the process of creating activated or customized biochar [5]. Customized biochar is a derivation of pristine biochar that has its physiological and biochemical features (e.g., specific surface area, porous nature, ion exchange potential, surface active sites, pH, etc.) and adsorption potential improved by biochemical processes for its efficient performance in the electrodes of microbial fuel cells. The majority of biochar engineering approaches in microbial fuel cells are more practical or least costly than traditional carbon activation procedures [6].

This review describes some of the implementations of biochar in microbial fuel cells (MFCs). Brief information on the synthesis of biochar along with characteristic features of the biochar applied in the MFCs. The paper also depicts the challenges and prospects associated with the large-scale application of biochar as a way to combat global warming and climate change in future.

2. Biochar

2.1. Introduction to microbial fuel cells

Industrialization and rapid growth of population are highly dependent on clean surroundings and a regular supply of electricity. MFC is a sustainable and environmentally friendly technology that fulfils the aforementioned needs by utilizing microorganisms. An MFC usually incorporates a proton exchange membrane (PEM) by distinguishing the anode from the cathode. The efficiency of MFC depends on the electrodes used [7]. The primary premise of a fuel cell is the direct conversion of chemical energy from a fuel into electrical energy rather than combustion. In MFCs, the organic substrates present in wastewater undergo microbial oxidation. An ideal MFC consists of two electrodes – anode and cathode which are divided by a PEM, made of Nafion or polytetrafluoroethylene (PTFE).

Organic compounds like acetate and glucose are oxidized in MFCs to generate electrons, which flow down to an external circuit and generate electricity. Organic compounds are oxidized anaerobically in MFC, resulting in the liberation of protons, electrons, and CO_2. The cathode is where water is generated by the reduction of protons and electrons using oxygen supplied from outside. The liberated protons and electrons pass through a medium, which is an electrical circuit for electrons and a membrane for protons, to enter the cathode. The formation of water in the MFC is depicted by the equation below [8].

$$CH_3COO^- + 4\ H_2O \rightarrow 2HCO_3^- + 9\ H^+ + 8\ e^-$$

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H \qquad 2O$$

The anode of a MFC undergoes oxidation, while the cathode undergoes reduction (Fig. 1). This oxidation and reduction create the potential difference between the electrodes, resulting in the generation of bio-electricity.

In MFC, biochar can serve as solitary electrodes, electrocatalysts and material for PEM [9]. If biochar is to be used as an anode, it must exhibit high porosity and a large surface area. It should also have a high carbon content and be an excellent conductor of electricity. Other key requirements are non-biodegradability, biocompatibility and economic feasibility. It needs to be cost-effective, highly porous and possess a negative surface charge. As a cathode catalyst, biochar should be cost-effective, have porosity and large surface area. Pyridinic, pyrrole, and graphitic nitrogen should all be present and ORR should be enhanced

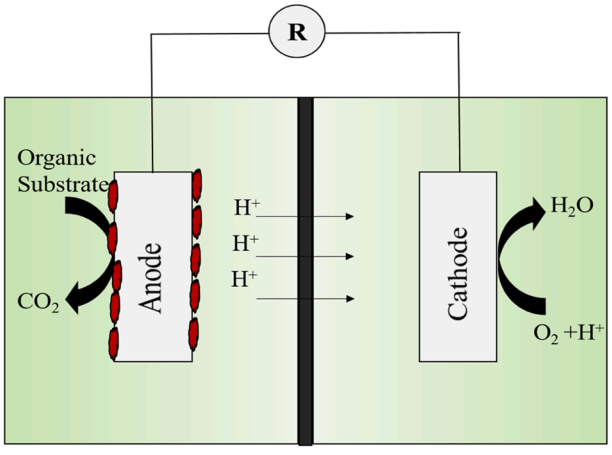

Fig. 1. General mechanism of microbial fuel cells.

[10].

2.1.1. Electrodes in MFC

For MFCs to operate well in terms of bacterial adhesion, electron transfer and electrochemical efficiency, the electrode material must be selected carefully. In MFC, the expenses of materials must be low and power densities must be high. Furthermore, the cathode materials should have catalytic characteristics for the reduction of oxygen. Electrodes must display the following characteristics:

- High surface area and porosity
- High electrical conductivity
- Stability, durability and economic feasibility
- Biocompatibility

Owing to its flexibility, abundance and low cost, carbon is the most suitable material for MFC electrodes. It exists in various structures and surface areas. Hence, carbon can be adopted in any type of MFC. Carbon electrodes have better anodic potential and allow scans to more negative potential than platinum or gold electrodes [11].

2.1.2. Implementation of biochar in MFCs

Biochar is an example of a low-cost substance with a multitude of uses. Locally available biochar, such as agricultural and forestry wastes have lower feedstock procurement, extraction, and transportation costs. Biochar is ten times cheaper than GAC and GG, ranging from 51 to 381 US$/ton. In light of the many features of biochar, in MFC, biochar can serve as solitary electrodes, electrocatalysts and materials for PEM. Numerous alterations of commercialized electrodes and PEM have been investigated to assure the long-term viability of MFC [12]. Substances obtained from waste have been a popular choice for such improvements, and biochar is such a substance that can be used to make a variety of MFC elements [13]. Although, Biochar is adopted as an anode, cathode, PEM, or cathode catalyst in MFCs. Therefore, the same parameters that apply to the anode also apply to the cathode. The property of cation exchange is critical for biochar as a PEM. The implementation of biochar in MFC is depicted in Fig. 2 [14].

2.2. Synthesis of biochar

Biomass is mostly made up of cellulose, hemicellulose, and lignin, with minute quantities of pectin, protein, extracts, and ash [15,16]. Biochar is a carbonaceous by-product formed when biomass is thermally converted in an anoxic atmosphere. The general synthesis of biochar is represented in Fig. 3.Fig. 4.

There are various methodologies to obtain biochar effectively. Pyrolysis is one of the techniques that produce energy with a significant fuel-to-feed ratio [17,18]. The various raw materials of biochar production along with their application in microbial fuel cells are listed in Table 1.

Biochar is made from various raw materials, including lignocellulosic biomass, microalgae, and culinary wastes like banana peels and watermelon skin. Biochar precursors have also been investigated using sewage sludge and organic fractions from landfills. Biochar is created at temperatures ranging from 300 °C to 700 °C and for several durations, generally 1–2 h [19]. Certain researchers processed the organic precursor during biochar formation to expand the surface area, porosity, and to lower the metal content [20].

Pyrolysis is the process of burning the biomass in an inert medium at elevated temperatures of about 300 °C-900 °C [29]. Biomass experiences a sequence of processes during pyrolysis to yield biochar, bio-oil, and syngas, which are solid, liquid, and gaseous phase compounds, respectively. The reaction temperature, rate of heating, and residence duration are all parameters that influence the yield of pyrolysis. The pyrolysis mechanism is categorized into three types depending on the heating rate: slow pyrolysis, fast pyrolysis, and flash pyrolysis (Table 2) [30].

Pyrolysis vapour persists in the reactor at lesser temperatures (400 °C–600 °C) with a lengthy vapour residence period in slow pyrolysis. The temperature range of fast pyrolysis is analogous to slow pyrolysis when the heating rate is more than 200 °C min^{-1}, and the residence period is substantially shorter than slow pyrolysis. Fast pyrolysis is commonly utilized to produce large amounts of bio-oil while reducing the production of charcoal [31].

Other methods used in the production of biochar include hydrothermal Carbonization, flash carbonization, torrefaction, gasification, etc. **(**Table.3**).**

Hydrothermal Carbonization (HTC) produces hydrochar by heating feedstock to 200 °C–300 °C in a sealed container under autogenous pressure of 2–10 MPa in the presence of water [32]. Hydrochar has a lower carbon and ash percentage than biochar and a smaller pore volume. On the other hand, the flash carbonization method generates biocarbon, particularly charcoal from biomass rapidly and effectively, often by igniting and controlling a flash fire at high temperatures inside a packed bed (1 MPa) [33]. Charcoal yields are approximately 40% by weight.

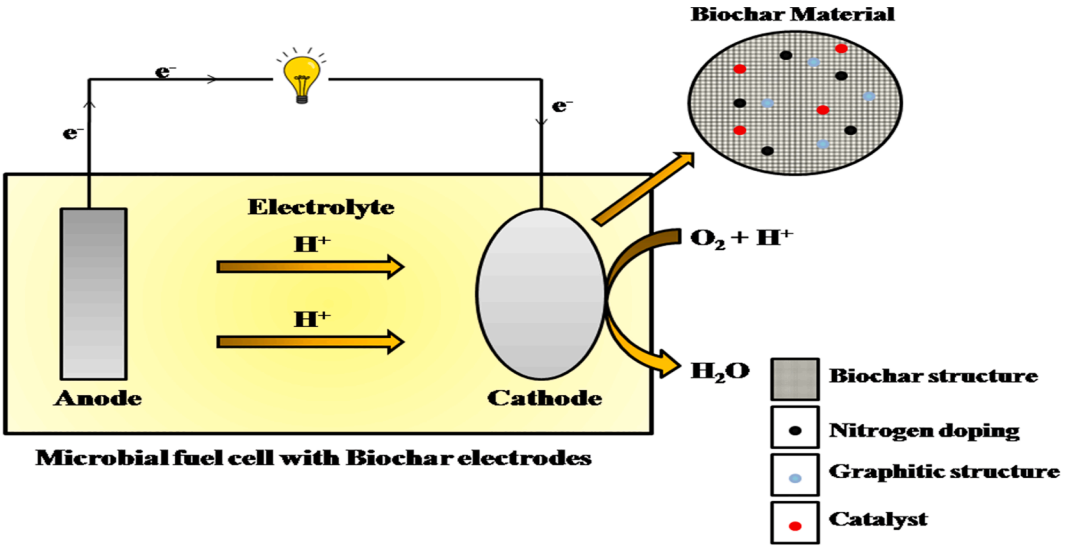

Fig. 2. Incorporation of Biochar Electrodes in MFC.

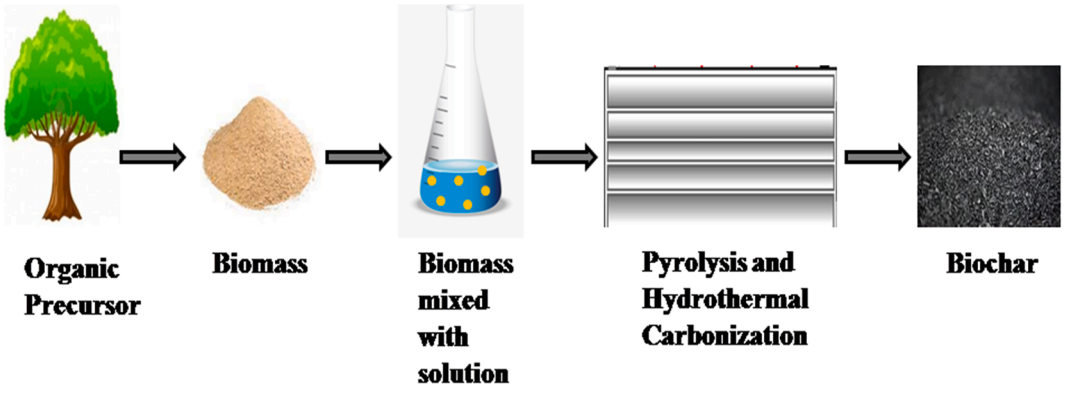

Fig. 3. Schematic representation of the synthesis of Biochar.

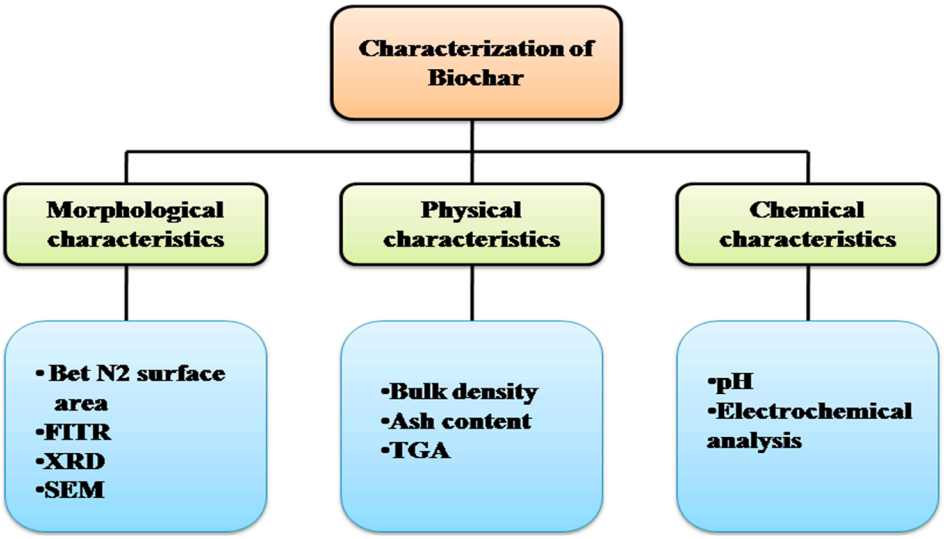

Fig. 4. Characterization of Biochar.

Table 1
Production of biochar and their implementation in MFCs.

Precursor for Biochar	Application in MFC	Method for activation	Pyrolysis temperature (°C)	Maximum Power Density	References
Sewage sludge	Catalyst in the cathode	———	900	500 mW-m^2	[21]
Compressed milling residue	Electrodes	———	1000	532 mW-m^2	[22]
Forestry byproduct	Electrodes	———	1000	457 mW-m^2	[22]
Wood biomass	Cathode	KOH	1000	146.7 mW-m^2	[23]
Corn straw	Electrodes	KOH	900	8.89 W-m^3	[24]
Corncob	Catalyst in the cathode	———	650	458.85 W-m^3	[25]
Watermelon skin	Catalyst in the cathode	HCl	700	0.262 W-m^3	[26]
Lignocellulosic biomass	Cathode	———	900	———	[27]
Rubber tree sawdust	Anode	———	500	3.26 μ W/m^3	[28]
Banana peel	PEM	H_2SO_4	600	41.08 mW/m^2	[14]

Table 2
Types of pyrolysis with biochar production rate.

Conditions	Slow pyrolysis	Flash pyrolysis	Fast pyrolysis
Temperature (°C)	300–700	800–1100	550–1000
Heating rate (°Csec^{-1})	0.1–1	<1000	10–200
Vapor residence time (Sec)	~ 500	<0.5	between 0.5 and 1
Particle size (mm)	5–50	<0.2	<1
Biochar production (wt%)	30	12	20

Before pyrolysis or gasification, torrefaction is a mild pre-treatment method having a temperature in the range of 200 °C–300 °C, moderate heating rate, and lesser retention period [34]. The resulting solid material is frequently carbon-rich, porous, and of low density, making storage and transportation easier. Another method for biochar production is the gasification process. At high temperatures of about 800 °C, gasification converts carbonaceous substances into syngas, tars, and char in the presence of an active gaseous medium such as O_2, N_2, air, and CO_2 [35]. Char accounts for only 5–10% of the feedstock mass.

Table 3
Different methods for the production of biochar.

Type of Biochar synthesis process	Temperature used.	Type and amount of biochar formed	References
Pyrolysis	300 °C–900 °C	Biochar	[29]
Hydrothermal Carbonization (HTC)	200 °C–300 °C	Hydrochar	[32]
Flash carbonization method	Fire high temperature	Charcoal (40% by weight)	[33]
Torrefaction	200 °C–300 °C	The substrate material of Biochar	[34]
Gasification	800 °C	Char (5–10% of the feedstock mass.)	[35]

2.3. Characteristics of biochar and biochar catalysts

The physical features of biochar, including pore size, surface area, density, etc. are substantially influenced by the pyrolysis temperature [36]. Biochar is made from various ingredients and modified for various applications. For example, large surface area, biocompatibility, tolerance to corrosion, lower ohmic, and higher electrical conductivity are all parameters for use in the anode [37]. Apart from these characteristics, a material's toxicity, hydrophilicity, cost, and chemical stability are the factors that influence its appropriateness as an anode [38].

Decreased charge transfer resistance, large surface area, the existence of heteroatoms for enabling delocalization of charge, higher current density, and lower activation barriers are the electrochemical features of the cathode components that are preferred for improving ORR [39]. Furthermore, when used as a cathode catalyst, qualities such as good material stability and economic feasibility are preferred. In this article, the features that make biochar suitable for each application have been matched to features of biochar. Higher porosity and surface area of the electrode or catalyst increase the likelihood of the redox pair forming on the electrode, i.e., microorganisms in the case of the anode and TEA in the case of the MFC cathode [40]. As a biocompatible base media biochar's large surface area encourages the growth of microorganisms [41,42].

The biochar's electron-giving ability and the surface area also help the biofilm perform better [43]. Biochar's biocompatibility makes it an excellent component for anode [44]. Electrical conductivity of Biochar, which allows for improved synergy between the surroundings and bacteria, can help with anode charge [45]. The extent of graphitization affects the electrical conductivity of carbon compounds. As the carbon achieves sp2 hybridization, graphitization of the biochar ensues, resulting in enhanced electrical conductivity due to increased electron mobility [46,47]. The porosity of the component is a significant quality of the cathode that promotes ORR, similar to the necessity for a large surface area in an anode. The presence of diverse N-groups in carbon compounds like pyridinic, pyrrolic, and graphitic N, improves the electrocatalytic efficiency of MFCs [48].

Biochar generated from various waste products, such as sewage sludge, orange peel, corncob, wheat straw, and so on, has the features listed above needed for efficient working of MFCs [49]. Biochar is a low-cost substitute to metals for use as electrodes or cathode catalysts since it is made from waste raw materials and has a simple synthesis procedure. To lower the MFC fabrication costs the use of waste-based materials for various components can save a lot of money (Table 4).

2.4. Biochar characterization

The mass percentage of moisture, volatile matter, ash, and fixed carbon can be determined via quantitative estimation. A quantitative estimation can be performed using standard procedures such as ASTM, ISO, DIN, and SB [55]. Other than quantitative estimation, analytical techniques including an elemental analyzer are commonly used to evaluate the elemental content of biochar. The main components of biochar are carbon, hydrogen, oxygen, and sometimes nitrogen. Conventional biochar has a carbon percentage of 45–60 wt%, 2–5 wt% of hydrogen, and 10–20 wt% of oxygen. Biochar's characteristics are also influenced by the inorganic components it contains. Inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence (XRF), and X-ray diffraction (XRD) are three analytical methods that can be used to characterize inorganic components [56].

A broad spectrum of analytical methods are used to investigate the morphology of biochar. For basic examination of biochar like particle morphology and surface texture, scanning electron microscopy (SEM) and transmission electron microscope (TEM) are extensively employed [57]. The extensively adopted methods for assessment of the microstructure of biochar are XRD, Raman spectroscopy, and energy-dispersive X-ray (EDX) spectroscopy [58]. The Brunauer, Emmett, and Teller (BET) methods are applied to examine the surface area and pore structure, with N_2 and CO_2 being the most commonly utilized sorbate gases. For studies that do not depend on peak ratios, solid-state ^{13}C nuclear magnetic resonance (NMR) is an effective approach [59].

X-ray photoemission spectroscopy (XPS), FTIR, and temperature-programmed desorption (TPD) approaches can be used to determine the surface functioning, surface chemistry, and composition of biochar [60]. In the implementation of biochar as functional substances such as catalysts, adsorbents, and electrode materials, surface functional groups serve an essential role [61]. The notion that the biochar surface has a spectrum of hydrophilic and hydrophobic functional groups, both acidic and basic, contributes significantly to its reactivity.

2.5. Biochar modification

Conventional biochar generated through a thermochemical conversion mechanism have a restricted number of polar oxygenated surface groups including CO, C═O, and OH, and low porosity and surface area [62]. Biochar's widespread use as a functional component is limited by these innate drawbacks. For biochar intended to be employed as a catalyst or adsorbent, an abundance of surface functionality is particularly desired since it may give more functional sites for catalysis or pollutant adsorption. Biochar utilized as an energy storage medium or catalyst, benefits from porosity and wide surface areas, which allow significant mass transfer fluxes and active loading.

As a result, an appropriate modification technique is required to improve the efficacy of functionalized biochar components. The most common approach for producing oxygenated functional groups on the biochar surface is surface oxidation. Surface oxidation procedures can produce a variety of oxygenated functional groups, including carboxyl, phenolic hydroxyl, lactones, and peroxides [63]. The commonly employed surface oxidation reagents are H_2O_2, O_3, $KMnO_4$, and HNO_3.

Basic amino groups on the biochar surface have proven to boost their efficiency in capturing CO_2 and pollutant adsorption. An

Table 4
Characteristics of Biochar.

Source of Biochar	Surface area (m^2g^{-1})	Total pore volume (cm^3g^{-1})	Average pore size (nm)	Total acidity (mmol g^{-1})	References
Hardwood	1.9	———	———	2.6	[50]
Biochar (commercial)	838–949	0.9	3.2–3.5	1.7–2.0	[51]
Corn stover	10	0.05	———	0.95	[52]
Sewage sludge	18	0.02	4.1	———	[53]
Activated carbon (commercial)	1944	1.2	1.2	0.23	[54]

environmentally safe approach for biochar's surface animation is chemical alteration utilizing amino-containing chemicals. In solid acidic compounds, sulfonic groups (SO_3H) are the most common functional groups. For the catalysis of many chemical processes, they are commonly utilized as replacements for liquid acids [64].

When compared to activated carbon, one drawback of biochar compounds is that they frequently have limited micropores with a smaller surface area. Regulated porosity and an enormous surface area are extremely beneficial for implementations such as energy storage in supercapacitors, electrocatalysis, and CO_2 capture or H_2 storage. In situ catalytic pore development during biomass pyrolysis is an extensively utilized strategy for adjusting the pore structure of biochar. Certain compounds, such as $ZnCl_2$ and H_3PO_4, catalyze the reaction. $ZnCl_2$ was discovered to considerably enhance the surface area and porous capacity of biochar [65].

Post-activation pore structure tailoring was also employed to modify the pore structure. In most cases, the post-activation procedure consists of two steps - direct pyrolysis of the biomass to generate original biochar with a limited pore volume and surface area, and activation of the biochar using physical or chemical means to enhance its porous structure and surface area [66]. Physical activation using various oxidizing gases including air, O_2, CO_2 and chemical activation with KOH, NaOH, H_3PO_4, or $ZnCl_2$ are the most common types of post-activation. The chemical activation procedure entails heating a combination of carbon precursor and activating agent to temperatures between 450 °C and 900 °C [67].

Biochar-based nanocomposites can be endowed with hybrid capabilities as a result of the recombination of certain nanostructures on their surfaces, opening up potential implications in a variety of disciplines. Many applications of final nanocomposites have been demonstrated, involving catalysis, fuel cells, drug delivery and bioimaging.

2.6. Doped-biochar

To modify biochar characteristics for a wider range of applications, suitable engineering or alteration methods are generally necessary, but the regulated insertion of active sites on biochar remains a challenge. In recent years, metal-free heteroatom doping has become popular in carbonaceous communities. On artificial nanocarbons, doping procedures with earth-rich elements like sulphur, nitrogen and boron were thoroughly tested. Generally, introducing exogenous non-carbon atoms into the organized sp2-hybridized carbon backbone can change the electrochemical capabilities of the native -electron networks, resulting in an uneven electroactive state that is required for more electrocatalysis [68]. To promote the catalytic nature of nanocarbons, increase the limit of detection of sensors, and enhance nanomaterial dispersion, researchers used heteroatom doping techniques, particularly nitrogen doping (N-doping), which has the highest efficiency (Fig. 5).Fig. 6.

2.6.1. Nitrogen-doped biochar

Heteroatom-doped carbon nanotubes have been used as ORR electrocatalysts in chemical fuel cells since the foundation of nitrogen-doped carbon nanotubes with significant catalytic ORR behaviour in an alkaline solution. According to current investigations, metal-free N doped carbons' ORR catalytic capabilities outperform generally accessible Pt catalysts [69]. Various N-groups in carbon structures, such as pyrrolic, pyridine and graphitic N boost the electrocatalytic efficiency of MFCs. Pyridinic N not only has a lone electron pair, but it also transmits an electron to the conjugated π bond, speeding up the ORR by boosting reductive oxygen adsorption [70]. Zhong along with his coworkers developed an inexpensive and environmentally friendly method for making nitrogen-doped hierarchically porous carbon from nitrogen-rich, highly robust watermelon rinds, which they used as an electrocatalyst in air–cathode MFCs. They discovered that after activating watermelon peel in HCl at 700 °C, the produced biochar was rich in C–N bonds, with large graphitic and pyridinic N concentrations. The result is that the ORR's electrochemically active region via the four-electron pathway was massive (658.9 m^2g^{-1}) [26]. The ability of porous nitrogen-doped biochar (AMBC) bead sorbent to remove CO_2 was examined in this study. The AMBC beads have a well-developed porous structure and a large specific surface area of 328.6 m^2g^{-1}, which is beneficial for CO_2 adsorption. The CO_2 removal efficacy was increased further by enhancing the pore density and large surface area of the sorbent in adsorption tests conducted on a pilot-scale fixed-bed column. The CO_2 elimination capacity of the synthesized AMBC beads was 10.15 mmol g^{-1} at 20 °C, which was significantly greater than that of generally used activated carbons and other adsorbents. The conveniently retrieved AMBC beads can be employed as a CO_2 capture adsorbent that is both efficient and environmentally benign [71].

2.6.2. Heteroatom-doped biochar

The total active area of the electrocatalyst increases as more surface catalytic sites are subjected to oxygen molecules. Because of their high porosity, activated carbons have a considerable interior surface area, varying from 500 to 2000 m^2g^{-1} [72].

Liu et al. used cellulose to make N and P dual-doped carbon, which they used as an effective electrocatalyst in an air–cathode MFC. The energy output was higher than that of the frequently used Pt-C catalyst (2293 ± 50 mW-m^2 compared to 1680 ± 32 mW-m^2) in MFCs [73].

One of the studies used MFCs with an alfalfa leaf carbon cathode to

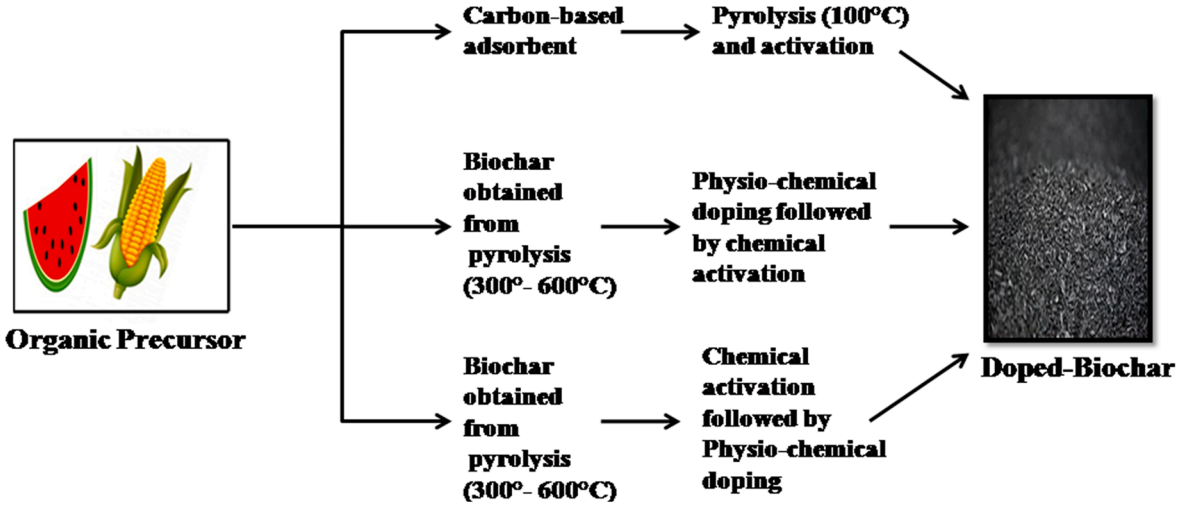

Fig. 5. Different methods for production and activation of biochar.

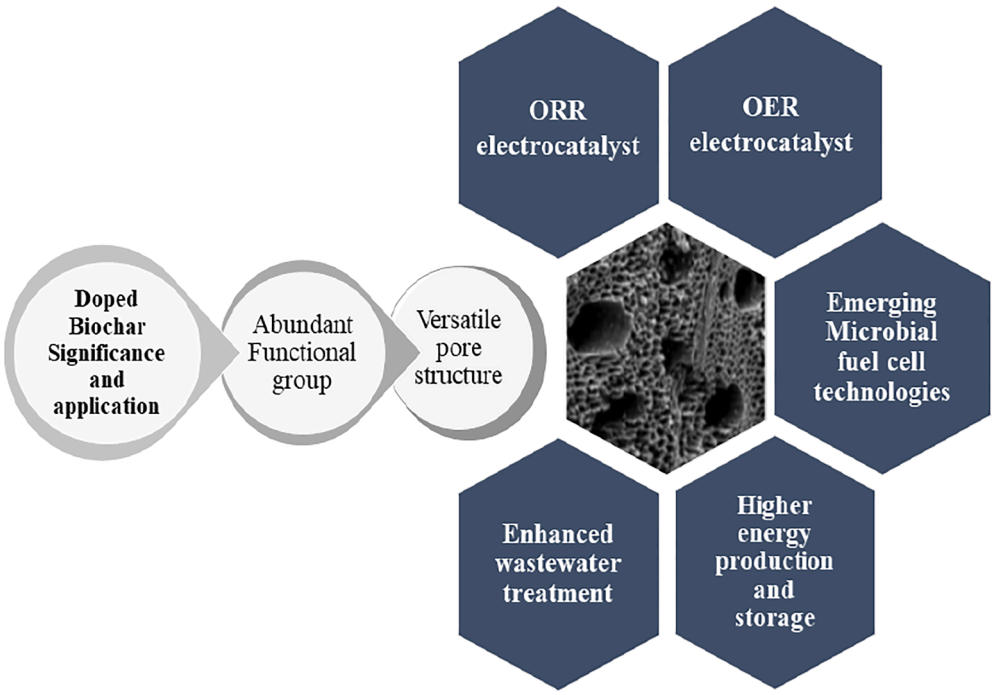

Fig. 6. Illustration of significant properties of doped biochar and its application.

produce high cathodic catalytic activity and high efficiency. The achieved energy output was around 1328.9 mW-m^2, which was greater than that of Pt-C. They also discovered that chemical activators increased the ORR and MFC energy output by affecting the catalytic activities of carbon substances obtained from alfalfa leaves. The remarkable electrochemical performance of the carbon material generated from KOH-activated alfalfa leaves was associated with the elevated quantities of pyridinic N, graphitic N, and C–P capabilities [74]. Furthermore, metal and nitrogen atoms doped into carbon lattices can change the carbon's electrical and geometric properties, boosting ORR catalytic activity. Huang et al. exhibited ORR catalytic efficacy in carbon substances generated from sewage sludge with a spatial porosity. They also discovered that doping the carbonized sewage sludge composite with Mn and N components improved the ORR catalytic activity [75].

2.7. Estimation of biochar

A biochar electrode's morphological features and catalytic efficacy is

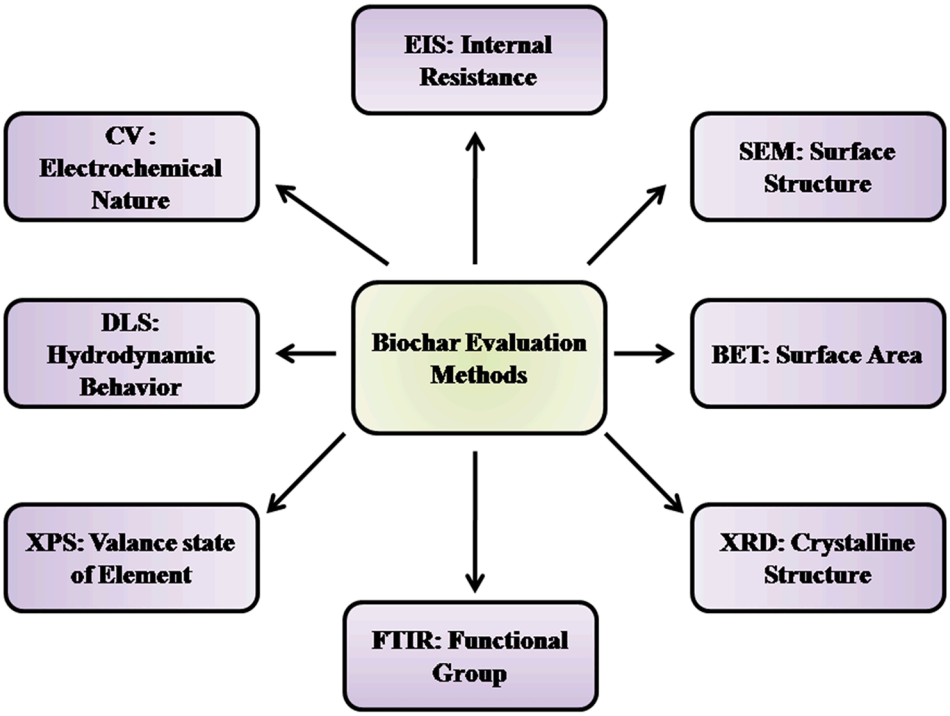

Fig. 7. Different methods for evaluating Biochar.

determined by assays. The ORR of electrons and their acceptors is affected by the cathode voltage. Various standard analytical procedures, such as CV, electrochemical impedance spectroscopy, and scanning electron microscopy, can be utilized to examine biochar from a broad perspective. The different methodologies for estimating the biochar are displayed in the figure. A triple-electrode framework with an operating electrode, a counter electrode, and a reference electrode is used to conduct CV and EIS studies. Ag/AgCl and Hg/Hg_2Cl_2 are two common reference electrodes. The various methods for evaluating biochar are portrayed in Fig. 7.

Chen et al. (2019) tested the cathode in an abiotic electrochemical cell utilizing a triple-electrode framework with an Ag/AgCl reference electrode and a 100 $mmolL^{-1}$ nitrogen-saturated PBS electrolyte. Khajeh et al. (2020) used EIS and CV to predict the electrochemical behaviour of an altered electrode. Their electrolyte is a combination of 10 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 0.1 M KCl, and their reference electrode is a normal calomel electrode, i.e., Hg/Hg_2Cl_2 [76,77].

CV is accomplished by altering the voltage (V) and scan rate (mVs^{-1}) at predetermined intervals. EIS studies under open-circuit potential circumstances investigate the internal charge–discharge transfer kinetics and diffusion resistance of electrolyte ions. By striking the sample with an electron beam, SEM shows surface morphologies such as texture, coarseness and porosity as well as the electrode architecture. The working electrode resultant current in a device is calculated using CV, a potentiodynamic electrochemical technique that introduces potential. The biocatalytic capabilities in biofilm anodes are evaluated using CV in microbial electrochemical systems (MESs), which also describes changes in electrochemical activity after the transfer to MES. The electrons created during voltammetry are driven into and out of the cells because electrode potential varies within a specific region, creating oxidation and reduction activity for each redox centre accessible to the electrodes.

Electrochemical impedance spectroscopy (EIS) has long been a prominent and dependable method of detecting internal resistance in a system; the spectrum of impedance at the electrodes provides useful data for understanding electrochemical reactions. EIS is generally utilized to examine the formed biofilm and recognize reaction kinetics to explain the electrodes' substrate features. EIS is particularly advantageous for certain upgrades such as charge transfer, ohmic, and diffusion transfer resistance in the current interruption and curve method, and can be assessed independently. EIS uses the features of a potentiostat to evaluate fluctuations throughout a frequency range of 100 kHz to 1 MHz. Furthermore, a frequency response analyzer uses the same method to analyze current and cell potential fluctuations; readings are expressed using Nyquist or Bode graphs. A Nyquist plot displayed negative hypothetical impedance (Z00) in comparison to the initial impedance (Z0); for a certain frequency, every place in the map signified impedance. Nyquist plots have one major flaw: they don't show the initial frequency used to detect a given spot. Resistance is formed at the maximum frequency, and Bode plots indicate impedance towards the X-axis frequency logarithm, as well as both the angle of the path and the actual impedance values, plotted on the Y-axis. e- differences reflect polarization resistance, and bode plots enable effective low- or high-frequency data analysis. Diffusion is demonstrated in the construction of an identical circuit by a Warburg element linked in parallel to a resistance solution or polarization resistance.

3. Applications of biochar in MFCs

The possibility of using biochar as cathode, anode, cathode catalyst, and base substance for PEM in MFC are explored and highlighted in this paper. Biochar may be a durable substitute to conventional electrodes, according to a review of the literature. However, numerous concerns, such as formulation process standardization, price evaluation for bulk generation, practical characteristics, and efficiency in contrast to the conventional substances, have yet to be resolved. Because the effort to adapt and build biochar-based electrodes, cathode catalysts, and membranes for MFC is still recent, there are large numbers of opportunities for detailed investigation into potential developments [78]. Different materials of biochar used as electrodes in MFCs are displayed in Table 4.

3.1. Biochar as electrodes

Biochar can be potentially used as a sustainable material for the production of highly efficient MFC. In most of the commercially available MFCs, the cost of electrodes employed in the system is 40–50% of the entire production expenses of the MFCs system. Biochar is a carbon-rich substance made by pyrolyzing biomass at extreme temperatures without or with limited oxygen. It has high porosity and a great surface area, both of which are good qualities for electrodes in MES [79]. To use the MFC in real-world applications, it is highly recommended to decrease the cost of electrodes and separators. Due to its porous nature, superior conductivity, and cost-effectiveness compared to other metal electrodes, commercially available activated carbon electrodes have been developed as alternative electrode material in MFC [80]. Biochar has less cost with a prominent carbon concentration and a large surface area, which includes macroporous, mesoporous, and nanoporous biochar [81]. The findings emphasize the usage of biochar as electrodes in MFCs to enable wastewater treatment and electricity generation simultaneously. Numerous studies are needed to employ biochar as an electrode and separator material in MFCs to overcome the limitations associated with biochar. Table 5 illustrates different biochar electrode materials used in MFCs.Table 6.

3.1.1. Biochar as anode

Biochar can also be utilized in MFCs as an inexpensive anode material (MFC). However, MFC's commercialization is hampered by its expensive nature and the non-renewable characteristics of its electrode materials. Granular activated carbon or graphite granules are the most common electrode materials utilized in MFCs. For instance, Granular activated carbon and graphite granules cost between $500 - $2500 t^{-1}, making them prohibitively expensive on a wide scale. Biochar has been discovered to be a viable and inexpensive replacement material for MFC. When the expenses and energy generated by wood-based biochar electrodes were compared to activated carbon and graphite electrodes, biochar (532–457 $mW\text{-}m^2$) was found to be equivalent to activated carbon (674 $mW\text{-}m^2$) and graphite (566 $mW\text{-}m^2$). Biochar, on the other hand, had a power output cost of $17–$35-W, which was 90% less than activated carbon ($402-W) and graphite ($392-W) [82].

In a study, biochar were produced by carbonizing forestry and milling residues at 1000 °C were employed as an anode in MFCs [22]. Further efficiency of the MFCs with biochar as electrodes was evaluated against MFCs encompassed with graphite and activated carbon anodes. It was observed that power obtained by using milling residue was 532 $mW\text{-}m^{-2}$ while that of forestry biochar was 457 $mW\text{-}m^{-2}$. On the other hand, the power density obtained while employing activated carbon in the MFCs was 674 $mW\text{-}m^{-2}$ which was maximum amongst all the other electrodes used. The maximum efficiency of the MFCs with granular activated carbon was owing to its large area and comparatively low internal resistance (40 O). Conversely, internal resistance offered by the forestry and milling biochar was 1.075 and 1.15 times more than granular activated carbon electrodes. However, the cost-effective nature of the biochar has resulted in the reduction of the cost of the process by ~90%. The result of the experiment demonstrated that at elevated temperature, the density of the pores was increased which in turn led to the exposure of high surface area of the anode during the process of power generation. However, further evaluation is needed as the lab-scale results can't be considered as characteristic of the biochar for large-scale energy generation.

A new biochar air cathode with a typically porous structure and high oxygen reduction reaction (ORR) activity was proposed, which was made by pyrolyzing Balsa Wood chips at 800 °C [83]. The biochar chips

Table 5
Different materials of Biochar used as electrodes in MFCs.

The function of Biochar in MFCs	The material used to produce Biochar	Power generated	Role in pollutant removal and efficiency of Biochar	References
1. Anode	Wood-based biochar	532–457 mW-m^{2}	NA	[82]
	Carbonizing forestry and milling residues	milling residue: 532 mW-m^{-2} forestry biochar: 457 mW-m^{-2}	NA	[22]
	Sawdust-based biochar	3.2 mA-m^{-3}	elimination of COD (90%) and sulphate ions (88.26%)	[28]
	Biochar modified with $NiFe_2O_4$/PEDOT	1200 ± 60 mW-m^{-2}	COD reduction: 28 ± 8.8%	[86]
2. Cathode	Biochar produced from banana plant stem and activated with KOH	528.2 mW-m^{-2}	NA	[93]
	Watermelon peel Biochar	0.262 W-m^{3}	NA	[95]
	Wood-based graphitic biochar modified with manganese oxide	187.8 W-m^{2}	NA	[23]
	Semi-carbonized Alfalfa leaves Biochar altered with KOH	1328.9 mW-m^{2}	NA	[96]

Table 6
Cost analysis for various cathode catalysts.

Sr. No.	Cathode catalyst	Cost for catalyst	Cost for catalyst + MFCs	Reference
	Platinum (Pt)	$ 150	$ 780–1340	[108]
	Fe-AAPyr	$ 3.20–3.40	$ 215–296	[109]
	Fe-Mebendazole	$ 3.40–3.60	$ 262–329	[110]
	CoNPc	$ 0.0114	———	[111]
	MnO_2	$ 3.84	———	[112]
	Biochar	$ 1.29	———	[112]

can be used as an air cathode in the MFC without the use of costly catalysts, binders, or gas diffusion layers. The biochar air cathode attained a maximum power density of 200 mW-m^{2} in single-chamber MFC tests, which was comparable to the other biochar-based air cathodes. Furthermore, when they were utilized in soil MFCs, the findings revealed that chip thickness had an impact on the soil MFCs' efficiency. The soil MFC with typical carbon felt floating cathode provided the highest power output of 72 mW-m^{2}, which was 45% greater than the soil MFC with 3.5 mm biochar. These findings show for the first time that complete biochar chips may be used to make binder and catalysis-free air cathodes that are both productive and environmentally beneficial.

By using a simple carbonization procedure, kenaf, pomelo peel, and packaging were employed to create a 3D macroporous carbon-based scaffold in MFCs. Remarkably, the greatest average output of the pomelo peel electrode was 40.2 A-m^{2} (electrode width 2.20 mm, estimated area (0.96 cm^{2}), which was 19% greater than that of the kenaf electrode (32.5 A-m^{2}). It's reticular macropore structure (porosity 97%, pore size >100 mm) provided more releasing routes for EAB adhesion and substrate diffusion [14]. In this investigation, three types of organic matter were explored for the manufacture of conducting electrode materials using simple carbonization processes: king mushroom, wild mushroom, and maize stem. These electrodes' structure–reactivity interactions were investigated using an electrochemical redox probe ([Fe $(CN)_6$]3/4) and biofilm electroactivity. Inductance, CV, and chronoamperometry methodologies were used to assess the electrochemical and bioelectrochemical availability and accessibility of carbonized electrodes to investigate the electron transfer rate (Kapp), charge transfer resistances, oxidative energy output, and electroactive substituents. On a carbon electrode generated from the maize stem, the highest electrocatalytic current (i_{max}) was 3.12 mAcm^{2}. That's eight times more than a standard graphite electrode. Organic carbon anodes serve as a low-cost option for MFC due to their porous structure, excellent electron transfer velocity, and significant electroactive biofilm development.

An experiment studied the impact of waste obtained from wood biochar alteration on carbon cloth anode efficiency. To determine the optimal alternative, the impacts of biochar modulation and biochar granule size were evaluated. Different MFCs with varied anode particle sizes ranging from 2 mm to 10 mm were employed [84]. It was concluded that the particle size of biochar was seen to be inversely dependent on the power output of MFCs. Biochar possesses a negative surface charge which can inhibit the biofilm's adhesion. As previously stated, the use of metal-doped carbon electrodes is a useful approach to attain quick biofilm adhesion and efficient electron transfer as it provides an effective area for the adhesion and growth of microorganisms. Hence, the observations must be examined from a new angle by delving further into the electrode surface's enzymatic and electrophysiological attributes.

The wastewater produced from the rubber industry was treated with the MFC consisting of a sawdust biochar anode. The sawdust biochar anode generated energy of 3.2 mA-m^{-3} and simultaneously eliminated ~ 90% of COD and 88.26% of the sulphate ions. The higher energy output along with COD elimination is a result of a non-exogenous oxidation reaction at the surface of the anode [28].

In MFCs, a study looked at the possible advantages of utilizing biochar granules as a substitute to the conventional carbon felt anode [85]. Sandy loam soil was used to fill single-chamber cylindrical air–cathode MFCs. Rice plants of the cultivar FARO 44 (*Oryza sativa* L.) were cultivated in plant MFCs (PMFCs). PMFC's efficiency was tested against soil MFC (SMFC) that lacked rice plants. The greatest energy output was 41.41 mW-m^{-2} of the cathode surface over the 125 days of operation, and it was recorded in PMFCs with carbon felt anodes (PMFC-RCF). The power density was lower in PMFCs with charcoal anodes (PMFC-RBC), with the maximum value being 11.11 mW-m^{-2}.

A robust stand-alone anode was fabricated by nickel ferrite and poly 3,4-ethylene dioxythiophene [86]. Further, the physical structure of the anode was determined using SEM. It was observed that the biochar has a honey-combed structure with a uniform pore on its surface. The cationic chemical distribution over the fabricated biochar was examined using XRD. The homogenous distribution of nickel ferrite was seen on the anode surface. The existence of polymers leads to the proper generation of biofilm onto the biochar anode surface. The fabrication of biochar with nickel ferric also increased its conductivity and electron transfer potential. Additionally, the performance of biochar altered with nickel ferrite and poly 3,4-ethylene dioxythiophene was evaluated against the unmodified biochar and biochar with iron oxide. It was concluded that Biochar modified with $NiFe_2O_4$/PEDOT gave maximum power output (1200 ± 60 mW-m^{2}) which was two-folds higher than biochar with iron oxide and six times larger than that of non-altered biochar. Hence, the result of the study concluded that the biochar doped with the metal ions produces a much higher energy output than that of bare biochar.

MFCs were developed and tested to remediate landfill leachate while also generating power. An activated carbon anode and a biochar anode were evaluated in batch cycles utilizing landfill leachate as a substrate in absence of inoculation. A semi-continuous serpentine form was also considered. The peak voltage, the current produced, and power densities

of the batch cells with activated carbon and biochar showed no change in the average. Both batch (with biochar) and semi-continuous COD reductions were seen (28 ± 8.8% and 21.7 ± 12.2%, respectively) [87].

The anode material is a critical component of MFCs for enhancing energy density (Fig. 8). The use of nanomaterials in MFC anodes results in outstanding hydrodynamic qualities, such as increased surface area, enhanced electron transfer, and the development of electroactive biofilm; furthermore, the enhanced microbe-electrode contact improves direct current production. However, nanomaterial-based anodes have significant drawbacks, including complicated manufacturing and property degradation. In some ways, biochar is a good supply of anode materials [88].

3.1.2. *Biochar as cathode*

Considering the significance of electrodes in MFCs, selecting the right electrode material is an important part of the system's design. Scientists are continuously designing high-performance, cost-effective electrode materials without compromising the attributes of the appropriate electrode material [22] An electrode material with high electrical conductivity, biocompatibility, bacterial attachment, surface area, corrosion resistance, and the ability to manufacture in any desired form is considered the ideal anode material for MFC construction, while an effective cathode must have high conductivity and a high surface area to volume (S/V) ratio, be non-corrosive, and have the least fouling. Cathode efficacy is critical in the generation of power in MFCs. The ORR is the most prevalent cathode reaction. One of the most limiting aspects of MFC operation is the steady reduction of oxygen on the interface of carbon or graphite electrodes, which results in a significant overpotential reduction. Carbon paper, graphite chips, felt, and fabrics are commonly used in cathode materials such as air cathodes, undersea aqueous cathodes, and biocathodes (Fig. 9) [89].

Biochar made from wastewater, Alfalfa leaf, corncob, watermelon rind, and other waste materials has been used as the cathode catalyst in MFCs. Biochar can enhance the passage of H_2 ions and O_2 while functioning as a cathode catalyst due to its greater porosity and surface area, which can significantly improve the ORR. Furthermore, the inclusion of graphitic and pyridinic N with sp2 hybridization, as well as pyrrolic N with sp3 hybridization, in biochar increases the electron cloud concentration of the electrocatalyst [90]. Nevertheless, before biochar catalysts can be standardized for field use, several problems that have been raised must be resolved. At differential catalyst loadings, electrochemical comparison with conventional catalysts (such as Pt-C) is not feasible. Numerous studies have suggested that biochar that has been activated/ produced at elevated temperatures or chemically activated has a better electrocatalytic activity. In addition, the electroactivity of biochar produced at a lower temperature is reduced attributed to the prevalence of unpyrolyzed organic components [91].

In 2013, Yuan along with his coworkers studied the potential of activated biochar obtained from sewage as a cathode catalyst. It was observed that this activated biochar produced 500 mW-m^{-2} of power in the air cathode MFC [21]. Further in 2015, the experiment looked at the symbiotic impact of adding coconut shell to biochar during the manufacturing process to improve the electrical conductance of the biochar that would be exploited as a cathode catalyst. The efficiency of the biochar blended with coconut shells gave energy output up to 969 mW-m^2 [92]. The carbon content, physiological, and molecular structure of biochar were closely linked to the pyrolysis temperature in both studies, resulting in improved catalytic performance.

Biochar produced from banana plant stem and potassium hydroxide was employed as cathode catalyst in MFCs. Further, the efficiency of this activated biochar was compared with non-activated biochar. The energy output obtained by employing activated biochar was 528.2 mW-m^2, which was much greater than non-activated biochar (483.7 mW-m^2) owing to its larger active surface area of activated biochar [93]. Recently, Zhang along with his coworkers defined some advantages of using activated biochar impregnated with potassium hydroxide. It was stated that the versatility of charge on the cathode surface and electron transfer is highly related to the porosity and the number of ions available on the biochar cathode [94].

Corncob, a crop residue, was pyrolyzed at temperatures varying from 250 to 750 °C and used as a cathode catalyst in MFCs. The biochar produced at 650 °C had a large surface area, resulting in a large number

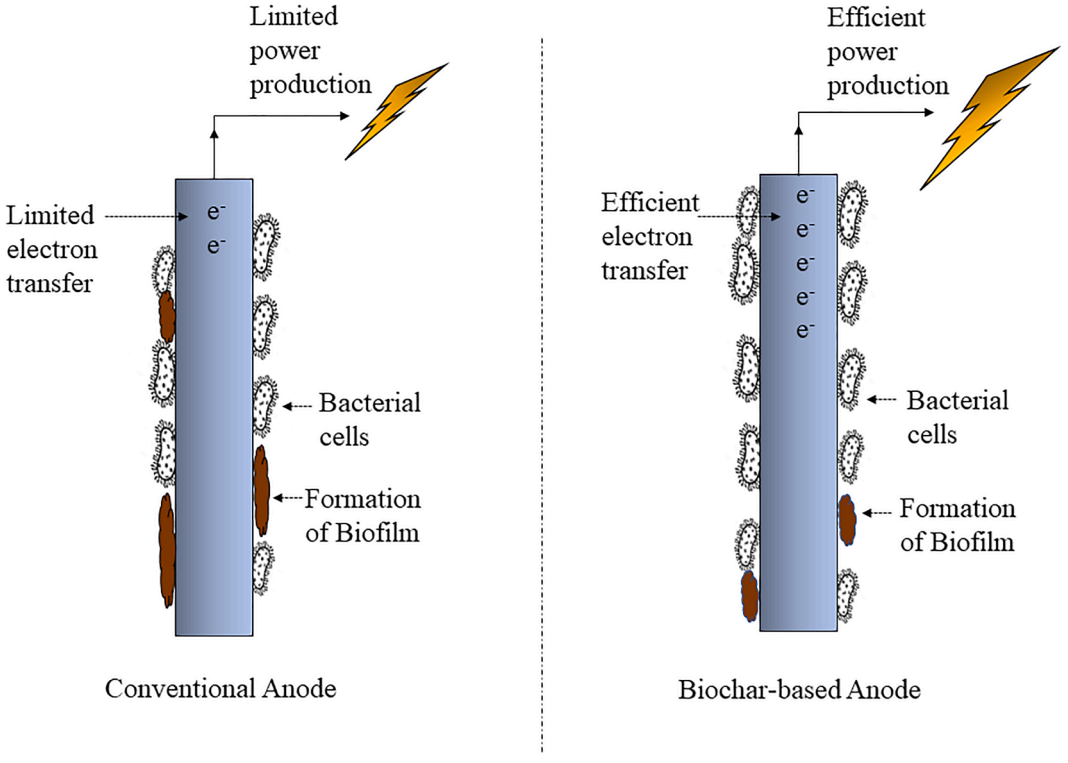

Fig. 8. Schematic representation of the application of biochar-based anode in MFCs.

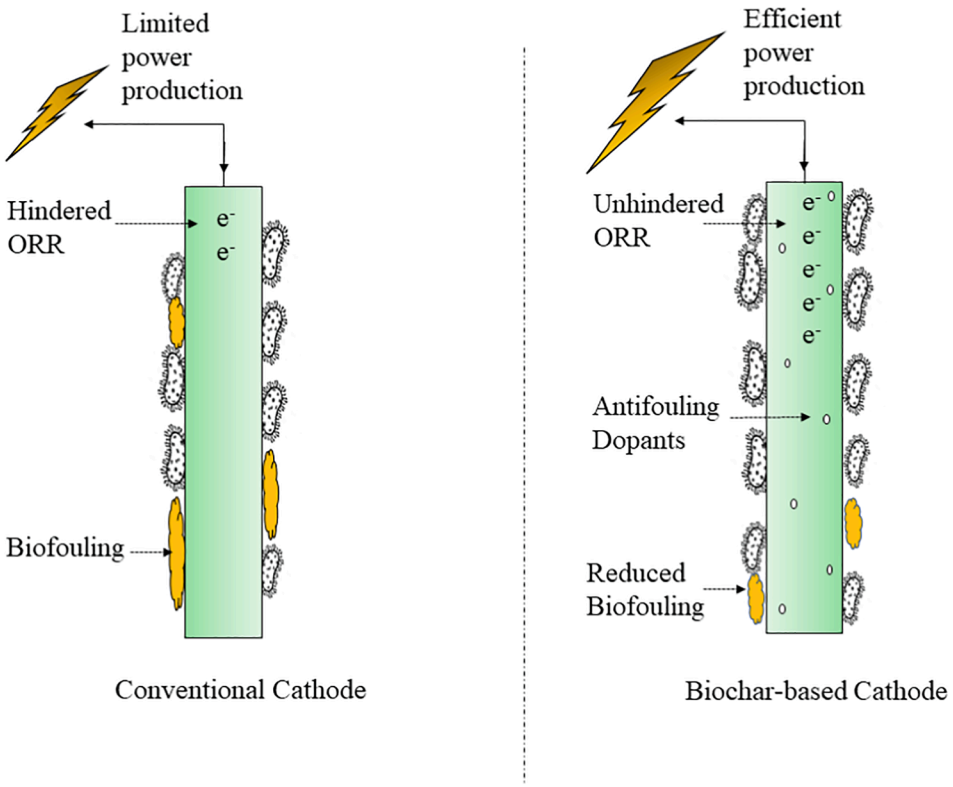

Fig. 9. Schematic representation of Biochar-based Cathode in MFCs.

of ORR sites. Besides the larger surface area, the availability of graphitic N and pyridinic N were the other important elements for biochar's electrocatalytic activity, as in previous studies. The method of activating biochar with KOH is well-known, and it results in an increase in porous nature and ionic concentration on the biochar surface, enhancing the movement of the surface charge and the electron cloud [14]. Cathode catalyst was made from semi-carbonized Alfalfa leaves and treated with three activation techniques (KOH, $FeCl_3$, and $ZnCl_2$) before ultimate carbonization at 900 °C to determine the efficiency of various activation techniques. According to the BET analysis, KOH activated biochar exhibited more prominent pores, resulting in a greater surface area (883.68 m^2g^{-1}) than all other activation techniques. The greatest energy output of MFCs using KOH-activated biochar catalysts (1328.9 mW-m^2) was equivalent to MFCs using Pt-C as a cathode catalyst (1337.7 mW-m^2) [14].

A nitrogen-rich raw material, watermelon peel, was processed to biochar to apply in MFC. Before pyrolysis at temperatures varying from 400 to 700 °C, the powdered watermelon rinds were rinsed in HCl. When the produced catalyst was applied to carbon cloth in an air cathode MFC at 700 °C, the highest power energy output was 0.262 W-m^3. The contrast of the fabricated catalysts to any existing carbon catalysts or Pt-C was exclusively used for electrochemical testing. The requirement of like comparison arises from the goal to find an inexpensive alternative to a high-cost standard Pt-C electrocatalyst [95].

High-temperature gasification and alkaline post-treatment (BCw) of wood-dependent biomass produced graphitic biochar (BC). The BCw was tested as a manganese oxide electrocatalytic base (MnO/BCw) and as an air cathode in an MFC. Physical, chemical, and electrochemical investigations were used to describe nanostructured MnO_2 crystals adsorbed on biomass-based graphitic sheets. With a current generation of 0.9 mA-cm^2, CV of MnO/BCw/Nafion inks revealed electrochemical characteristics of MnO_2. When compared to Vulcan Carbon (VC) (156.8 mW-m^2) and ma, BC showed excellently high current densities of 146.7 mW-m^2 (BCw) and 187.8 W m^2 (MnO/BCw) [23].

Cathode catalyst was produced from the leaves of semi-carbonized Alfalfa and processed with different activation techniques (Potassium hydroxide, Ferric chloride, and Zinc chloride) before complete carbonization at 900 °C to determine the efficacy of various activation processes [96]. According to the research, KOH-activated biochar exhibited more prominent pores, resulting in a larger surface area (883.68 m^2g^{-1}) than the other activation techniques. The highest energy output of MFCs using potassium hydroxide-activated biochar catalysts (1328.9 mW-m^2) was equivalent to MFCs employing Pt-C as a cathode catalyst (1337.7 mW-m^2). When employed as a cathode catalyst in MFCs at similar catalytic loadings, inexpensive metal-free biochar produced from organic material can achieve equivalent efficiency of Pt-C. The carbon activated with KOH had a greater concentration of N than the carbon activated with the other two techniques, according to XPS. In addition, activated biochar processed with KOH had a greater graphitic and pyridinic N content. It is a well-known phenomenon that these two forms of nitrogen play a critical role in improving ORR. Furthermore, the high-resolution P 2p spectra indicate maxima of the P–C and P–O groups, which have been linked to ORR.

3.1.3. Biochar used as both anode and cathode in MFCs

Chemical activation methods may be used to synthesize biochar, which can be applied in MFCs. Corn straw, crop residues, was utilized to create biochar at temperatures of 500 and 900 °C using KOH activation. Although this study demonstrates that MFC utilizing activated biochar as both anode and cathode can outperform commercial graphite felt in terms of performance, cathodic decomposition studies with Acid Orange 7 (AO7) show that biochar cathodes are unable to decompose the AO7. The existence of highly reactive species in biochar cathodes, which functioned as TEA rather than AO7, was identified as the cause [24].

On the other hand, numerous MFC-based cathodic dye biodegradation studies have found that the reactive oxygen species generated during the cathodic ORR are accountable for dye biodegradation. As a result, more researches are required to better characterize the surface chemistry of biochar electrodes used for dye degradation. However, when comparing non-activated biochar to activated biochar, it's

important to note that biochar activation has increased the surface area by 137 times.

Biochar was used to fill the gap between the anode and the cathode in a study to create a three-dimensional electrode MFC (3D-EMFC) [97]. The efficacy of 3DEMFCs treating nitrogen in contaminated water was studied using three kinds of biochar electrodes (biochar, biochar and zeolite combination, and MgO-modified biochar). The results indicated that 3DEMFCs with MgO-modified biochar had the greatest energy output of MFCs, at 4.45 ± 0.21 W-m^{-3}, and that the overall power output of 3DEMFCs (2.40 ± 0.28, ~4.45 ± 0.21 W-m^{-3}) was greater than that of MFCs without biochar (1.31 ± 0.24, 1.31 ± 0.24 W m^{-3}). Furthermore, 3DEMFCs with MgO-altered biochar had the greatest ammonium, total nitrogen, and COD removal potential (93.63.2%, 84.82%, and 91.61.3%, respectively), while MFCs had simultaneous short-cut nitrification and denitrification. Furthermore, SEM pictures revealed bacterial adherence to biochar, and the biofilm dry weights of MgO-altered biochar after the studies were the highest of three types of biochar electrodes, at 1034 mgg^{-1}. As a result, energy production and nitrogen elimination in 3DEMFCs were significantly improved, and biochar demonstrated good biocompatibility and unique electrochemical efficiency for MFC practical wastewater treatment applications.

Pyrolysis was used to convert contaminated water sludge to biochar, which is an effective waste reutilization method. The anode of an air cathode MFC was made of biochar, which was made from sewage sludge [92]. Before pyrolysis, the sewage sludge powder was adjusted with coconut shells in various weight ratios and cast into monoliths by mechanical pressing and calcination. The inclusion of coconut shells increased the total carbon content, which improved electrical conductivity. The introduction of 10 % coconut shell powder by weight to sewage sludge (SM-10) contributed to a maximum energy output of 1069 mW-m^{-2}, which was 2.2 times greater than the power density achieved without the introduction of coconut shell powder. The results showed that the electrodes' conductive nature was mostly related to the carbon concentration, which was increased owing to the introduction of coconut shell powder to the biochar. Even while the MFC with SM-10 anode had a greater power density, a closer look at the electrode material demonstrated that the graphite plate used for comparison had a far less surface area than biochar, making a genuine comparison impossible. To compare the performance, as compared to heteroatom doped commercial carbon powder formed into a comparable monolith was required.

The efficiency of an MFC was measured using a biochar electrode. After the carbonization process, electrodes were built of silicon, zinc, and copper in 40% quantity combined with generated waste coconut shell (CS) biochar materials [98]. In contrast to Graphite Particle (GP) (0.1920 m^2g^{-1}), the specific surface area of CS-Si (0.2532 m^2g^{-1}), CS-Zn (0.2025 m^2g^{-1}), and CS-Cu (0.2532 m^2g^{-1}) are greater. CS-Si (19.22 ± 0.5) mWm^{-2}), CS-Zn (26.40 ± 0.6) mWm^{-2}), and CS-Cu (47.04 ± 0.5) mWm^{-2}) had similar power production outputs to GP (32 ± 0.5 mWm^{-2}). The CS-Cu electrode delivers the highest power output and efficiency, according to test results. Metals enhance the surface area of biochar electrodes, which improves the efficiency of MFCs. For ecologically friendly systems, the CS-Cu electrodes are therefore viable, compatible, and least expensive.

3.2. Biochar in separators of MFCs

Large proton conductivity, minimal oxygen, and substrate crossover decreased biofouling rate, and other imperatives of successful PEM are reported in tandem by many studies attempting to create low-cost PEMs for use in MFCs. The fact that biochar possesses strong cation exchange properties, a high concentration of surface-active sides, and excellent porous nature supports its use in PEMs.

Expensive PEMs, such as Nafion-117, create a severe constraint in the technique's potential to expand sustainably. Production costs must be considerably decreased for an adequate field-scale implementation of MFC. This may be accomplished by employing an inexpensive PEM in MFCs that performs similarly to costlier widely viable PEMs. G-5, a new PEM containing 5% goethite and natural clay as a raw product, was synthesized and employed as a separator in MFC. The industrial Nafion-117 membrane, which is commonly used in MFC, was predicted to be five times costlier than the G-5 membrane [99]. The MFC with G-5 as PEM (112.81 ± 8.74 mW-m^2) had a somewhat greater energy output than the MFC with Nafion117 as PEM (106.95 ± 5.52 mW-m^2). In contrast to MFCs with Nafion-117 as PEM, COD elimination and Coulombic efficacy for MFCs with G-5 membrane were reported to be 22% and 8.6% higher, respectively.

In a study carried out by Neethu et al. (2019), it was discovered that the biochar-ceramic synthetic membrane had a lower oxygen diffusion coefficient than Nafion. However, because this study combines biochar with a ceramic membrane, the influence of biochar on proton conductivity was not evaluated separately [100]. Sulphonation of the matrix composites improves the interrelationship between the ions, allowing proton transmission to be facilitated.

Apart from proton conductivity, the energy output of MFCs utilizing biochar membranes (41 mW-m^2) was lesser than that of MFCs using Nafion 117 membranes (58 mW-m^2). Even after sulphonation, biochar cannot outperform Nafion with respect to their efficiencies as evidenced by the debate. When compared to Nafion membrane, however, the expense of biochar membrane is significantly lowered [101].

3.3. Biochar based catalysts

At the cathode surface, oxygen interacts with protons in the electrolyte and then electrons are transferred from the anode via metallic wire. This ORR on the cathode surface requires a large amount of energy. As indigenous cathodes absorb energy, energy production decreases. As a result, the cathode catalyst plays a critical role in the performance of MFCs, with the anode and cathode accounting for a major portion of the MFCs' construction cost. The efficiency of cathode catalysts is critical for a successful oxygen reduction process. In an MFC, the optimal cathode catalyst has effective ORR kinetics, is durable, has minimal over-potential activation, and is low cost. The oxygen reduction process at the cathode is regarded as a rate-limiting phase due to its heterogenic character. As a result, a very effective catalyst is necessary to minimize the cathodic overpotential. During the initial stages of the experiment, a premium noble metal dust platinum was employed; however, non-metal elements based on metal and carbon were used as an illustrative catalyst. Carbon-metal catalysts, as well as medium metal-nitrogen-carbon catalysts, were shown to be incredibly beneficial for ORR. In terms of power output, the efficiency of MFCs using various biochar-based ORR catalysts was evaluated.

Biochar has recently been recognized as a flexible medium for catalytic applications, prompting preliminary study into its catalytic activity and mechanistic principles in various pathways (Fig. 10). As a result, this topic describes the catalytic disadvantages and techniques of biochar in the field of catalysis, such as biodiesel synthesis, tar depletion in bio-oil and syngas (synthetic gas: H_2 and CO), enriched syngas development, biomass transition into chemicals and biofuels, deNOx reactions, and MFCs, to supply comprehensive details on the catalytic functions of biochar in the ground of catalysis.

Pt-based ORR catalysts are expensive, susceptible to biofouling, and quickly polluted by microbes, as previously stated. Researches look for inexpensive, catalytically active, biofouling-resistant system to increase the energy density of MFCs for these reasons [12]. Biochar is a carbon-based material that is commonly accessible. Porosity, wide surface, and high cation-exchange capacity are among the physical and chemical characteristics it provides. These characteristics improve the interplay between microbial development and essential nutrient cycles [102].

Due to their great surface area, chemical sustainability, superior electrical conductivity, and increased mass-transport potential, metal-

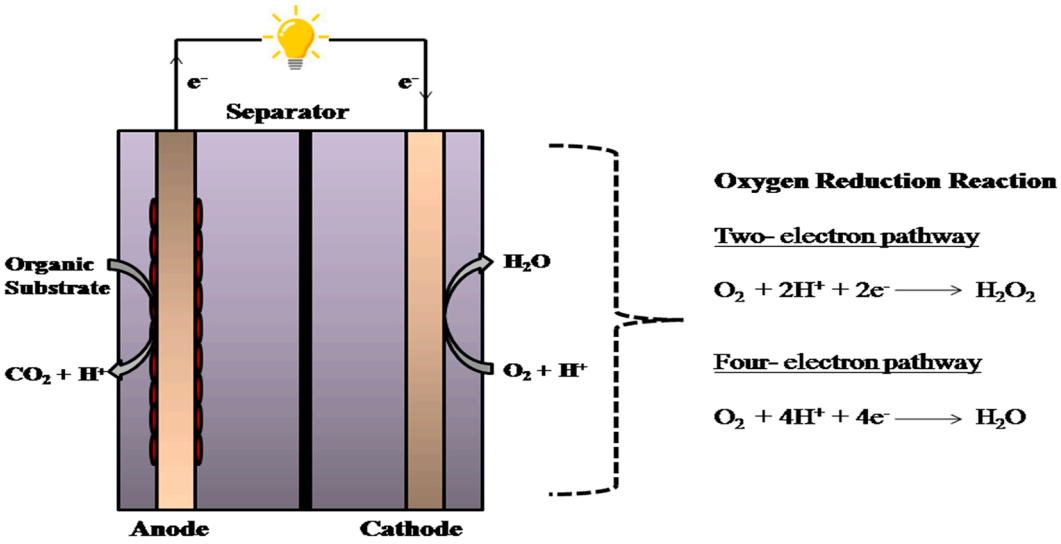

Fig. 10. Oxygen reduction reaction at the cathode surface.

free catalysts are potential options for MFCs. Biochar made from olive mill waste (OMW) either with or without supercritical CO_2 pretreatment, as well as salted pistachio nutshells, were generated in this study using pyrolysis, chemical, and physical activation. Using cyclic and linear sweep voltammetry in neutral solutions, the biochar's catalytic activity towards ORR was studied. In the case of reaction rate, the density of functional groups, and the number of electrons transferred, electrochemical analysis of the samples demonstrated that OMW biochar had the maximum catalytic activity toward ORR. This biochar was employed as catalysts in MFCs with an air cathode. The greatest energy output attained by MFCs with an OMW cathode was 271 ± 34 mW-m^2. This number was around 15 times greater than the energy output of a typical carbon black that was utilized as a control [103]. Even though the increased pyrolysis temperature will enhance energy utilization, the price would be greater than conventional biochar. Carbon-based electrocatalysts are less expensive than metals and are environmentally friendly [104]. At present, cost-effective biochar made from crop by-products shows significant ORR activity.

Sewage sludge (SS) biochar is a type of N- or transition metal-enriched, self-supported carbon, implying that it has an efficiency for ORR catalysis. For example, Yuan and colleagues have utilized SS biochar as an ORR catalyst in MFC. They discovered that the temperature of carbonization has a remarkable effect on the surface characteristics of biochar. The biochar contained numerous microspores, high N and Fe concentrations, and was highly active for ORR catalysis at 900 °C [21]. Another study used pyrolyzed livestock SS to create a hierarchically organized biochar with a honeycomb-like interconnecting macro-mesoporous framework. For the ORR, the synthesized catalyst had significant electrocatalytic activity, with the highest energy output of 1273 mW-m^2. In addition, the catalyst had recently had longer durability than the Pt-C cathode after 90 days of operation [105].

The synthesized catalysts might have a large surface area, porous nature, and a high graphitic N or S concentration, as well as good catalytic efficiencies concerning onset potential and energy output, as well as outstanding methanol poisoning resistance and persistence. A carbon nanoparticle-coated porous biochar (CNCB) made from Weisiopsisanomala was described by Zhou and colleagues. In comparison to other substances, the CNCB material had a higher surface area after carbonization at 900 °C. The CNCB had strong catalytic activity in the ORR, with an onset efficiency of 0.935 V, which was comparable to that of a commercial Pt-C catalyst, according to the findings (0.962 V) [106].

The scientists also employed pyrolyzed electroplating effluent as a potential catalyst for electrochemical CO_2 reduction in a MEC, as well as probable CO_2 reduction routes. CH_4, ethylene, CO, and acetate were the major products. They further stated that a non-metal chitin-derived carbon sheets (CS) bifunctional electrocatalyst for ORR was developed. When compared to commercial Pt-C catalysts, the CS demonstrated higher electrocatalytic activity, endurance, and bridging resistance [107].

The eggplant-derived hierarchical porous graphitic biochar was synthesized using a one-step technique. EPGC-800-2 was eggplant-derived biochar with K3[Fe(C2O4)3] [10]. 3H2O activation generated at 800C with a layered porous structure, large specific surface area (1137 m2 g1), and high graphitization degree. Later, the performance of the synthesized EPGC-800–2 catalyst was compared with Pt/C catalyst when employed in microbial fuel cells. EPGC-800-2 has a maximum power density of 667 mW m^2 in a microbial fuel cell, which is higher than Pt/C catalyst (621 mW m^2). EPGC-800–2 catalyst was shown to have a four-electron pathway towards ORR, with a higher n (3.90) and lower H2O2 yield (6.06%), as well as a high pyrinidic concentration MFCs which employed EPGC-800–2 catalyst exhibited elimination of ~ 80% COD from wastewater. The research revealed a green and simple method for producing excellent ORR catalysts from available biomass.

3.3.1. *Cost evaluation of cathode catalyst*

The catalyst value is a crucial issue in the expanding MFC sector. Platinum is a precious resource on the planet, despite the fact that it is impractical for potential growth. Biochar is an expensive and renewable resource. Table 5 gives a brief account of the cost analysis of various cathode catalysts.

4. Scope and future perspectives

Biochar demonstrated its potential application in microbial fuel cells by exhibiting remarkable advantages over many other traditionally used carbonaceous materials in MFCs. Large surface area, increased electrical conductivity, biocompatibility, chemical sustainability, and the existence of diverse active sites on the biochar surface are all significant characteristics for using biochar as an anode in Microbial fuel cells. Surface area, pore size, electrical conductivity, nitrogen content, a greater extent of graphitization and great fixed carbon concentration are the variables considered when determining the feasibility of biochar as a cathode in MFC. In the future, the feasibility of composites including biochar and other non-metallic substances for use in MFC should be investigated. Aside from advancements in the synthesis technique, future investigations should also include several operational changes.

Biochar has been shown to improve methane recovery in anaerobic digesters. By employing biochar-metal composites as electrodes to promote electro-Fenton type reactions, downstream processes including electrochemical oxidation of refractory chemicals in contaminated water are accomplished with fewer expenses.

The ORR has a substantial impact on Microbial fuel cell (MFC) performance. Furthermore, innovations for more sustainable, efficient, attainable, and cost-effective materials is necessary. ORRs benefit greatly from biochar's electrocatalytic capabilities. Several proposals are made for expanding the future development of biochar in MFCs. Although pyrolysis can yield biochar, there are no other methods for producing multiple-performance biochar that can be used in a variety of applications. The co-pyrolysis method, on the other hand, offers to increase the overall effectiveness of biomass pyrolysis by incorporating additional materials. As a result, co-pyrolysis can be used to improve the characteristics of biochar. Biochar has been widely studied as ORR electrocatalysts in the areas of fuel cells and zinc-air batteries. Apart from the ORR, additional emphasis must be placed on factors such as biofouling resistance, excellent conductivity, and long-term stability, all of which are critical for biochar-based MFC applications. However, there is a small date accessible in the existing literature in this regard.

Future research should include a life cycle analysis and a techno-economic estimation to evaluate biochar's viability as a novel green technology. MFC progress in the future will focus on commercial-scale conversion from the lab to real energy production applications.

5. Conclusion

Biochar is a remarkable renewable resource that can resolve many environmental challenges that have arisen in recent decades, such as pollution, remediation in soil, water, and atmospheric medium. Several studies in recent years have shown that biochar or biomass-derived carbon can be used as a free-standing electrode or as an electrocatalyst for the ORR in Microbial fuel Cells (MFCs). Because the push to adapt and build biochar-based electrodes, cathode catalysts, and membranes for MFC is still comparatively recent, there is significant scope for detailed investigation into future applications. Biochar was used as both anode and cathode in microbial fuel cells for the efficient removal of pollutants with simultaneous generation of electricity. Many researchers have demonstrated the potential of biochar in microbial fuel cells by experimental analysis of the remarkable properties of biochar including specific surface properties and higher conductivity. As a result, the biochar based-MFCs for wastewater treatment could be used as a pre-treatment to remove hazardous chemicals before biological treatment. Further, to determine the elimination methods of hazardous substances in biochar-based MFCs, a thorough investigation is required.

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CRediT authorship contribution statement

Sanchita Bipin Patwardhan: Writing – review & editing, Visualization. **Soumya Pandit:** Conceptualization, Writing – review & editing, Visualization, Project administration. **Piyush Kumar Gupta:** Writing – review & editing. **Niraj Kumar Jha:** Writing – review & editing. **Jyoti Rawat:** Writing – review & editing. **Hem C. Joshi:** Writing – review & editing. **Kanu Priya:** Writing – review & editing. **Meenal Gupta:** Writing – review & editing. **Dibyajit Lahiri:** Writing – review & editing. **Moupriya Nagg:** Writing – review & editing. **Vijay Kumar Thakur:** Writing – review & editing. **Kavindra Kumar Kesari:** Writing – review & editing, Visualization, Funding.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Oliveira FR, Patel AK, Jaisi DP, Adhikari S, Lu H, Khanal SK. Environmental application of biochar: current status and perspectives. Bioresour Technol 2017; 246:110–22. https://doi.org/10.1016/j.biortech.2017.08.122.

[2] Xiang W, Zhang X, Chen J, Zou W, He F, Hu X, et al. Biochar technology in wastewater treatment: a critical review. Chemosphere 2020;252:126539. https://doi.org/10.1016/j.chemosphere.2020.126539.

[3] Creamer AE, Gao B. Carbon-based adsorbents for postcombustion CO_2 capture: a critical review. Environ Sci Technol 2016;50(14):7276–89. https://doi.org/10.1021/acs.est.6b00627.

[4] Cha JS, Park SH, Jung S-C, Ryu C, Jeon J-K, Shin M-C, et al. Production and utilization of biochar: a review. J Ind Eng Chem 2016;40:1–15. https://doi.org/10.1016/j.jiec.2016.06.002.

[5] Ok YS, Chang SX, Gao B, Chung H-J. SMART Biochar technology—a shifting paradigm towards advanced materials and healthcare research. Environ Technol Innov 2015;4:206–9. https://doi.org/10.1016/j.eti.2015.08.003.

[6] Yao Y, Gao B, Chen J, Zhang M, Inyang M, Li Y, et al. Engineered carbon (Biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: characterization and phosphate removal potential. Bioresour Technol 2013;138: 8–13. https://doi.org/10.1016/j.biortech.2013.03.057.

[7] Elshobary ME, Zabed HM, Yun J, Zhang G, Qi X. Recent insights into microalgae-assisted microbial fuel cells for generating sustainable bioelectricity. Int J Hydrog Energy 2021;46(4):3135–59. https://doi.org/10.1016/j.ijhydene.2020.06.251.

[8] Jadhav DA, Carmona-Martínez AA, Chendake AD, Pandit S, Pant D. Modeling and optimization strategies towards performance enhancement of microbial fuel cells. Bioresour Technol 2021;320:124256. https://doi.org/10.1016/j.biortech.2020.124256.

[9] Li S, Ho S-H, Hua T, Zhou Q, Li F, Tang J. Sustainable biochar as an electrocatalysts for the oxygen reduction reaction in microbial fuel cells. Green Energy Environ 2021;6(5):644–59. https://doi.org/10.1016/j.gee.2020.11.010.

[10] Zha Z, Zhang Z, Xiang P, Zhu H, Zhou B, Sun Z, et al. One-step preparation of eggplant-derived hierarchical porous graphitic biochar as efficient oxygen reduction catalyst in microbial fuel cells. RSC Adv 2021;11(2):1077–85. https://doi.org/10.1039/D0RA09976G.

[11] Peera SG, Maiyalagan T, Liu C, Ashmath S, Lee TG, Jiang Z, et al. A review on carbon and non-precious metal based cathode catalysts in microbial fuel cells. Int J Hydrog Energy 2021;46(4):3056–89. https://doi.org/10.1016/j.ijhydene.2020.07.252.

[12] Palanisamy G, Jung H-Y, Sadhasivam T, Kurkuri MD, Kim SC, Roh S-H. A comprehensive review on microbial fuel cell technologies: processes, utilization, and advanced developments in electrodes and membranes. J Clean Prod 2019;221:598–621. https://doi.org/10.1016/j.jclepro.2019.02.172.

[13] Wang J, Wang S. Preparation, modification and environmental application of biochar: a review. J Clean Prod 2019;227:1002–22. https://doi.org/10.1016/j.jclepro.2019.04.282.

[14] Chakraborty I, Sathe SM, Dubey BK, Ghangrekar MM. Waste-derived biochar: applications and future perspective in microbial fuel cells. Bioresour Technol 2020;312:123587. https://doi.org/10.1016/j.biortech.2020.123587.

[15] Fabbri D, Torri C. Linking pyrolysis and anaerobic digestion (Py-AD) for the conversion of lignocellulosic biomass. Curr Opin Biotechnol 2016;38:167–73. https://doi.org/10.1016/j.copbio.2016.02.004.

[16] Masebinu SO, Akinlabi ET, Muzenda E, Aboyade AO. A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. Renew Sustain Energy Rev 2019;103:291–307. https://doi.org/10.1016/j.rser.2018.12.048.

[17] Demirbaş A. Analysis of liquid products from biomass via flash pyrolysis. Energy Sources 2002;24(4):337–45. https://doi.org/10.1080/00908310252888718.

[18] Fakayode OA, Aboagarib EAA, Zhou C, Ma H. Co-pyrolysis of lignocellulosic and macroalgae biomasses for the production of biochar – a review. Bioresour Technol 2020;297:122408. https://doi.org/10.1016/j.biortech.2019.122408.

[19] Zhang Z, Zhu Z, Shen B, Liu L. Insights into biochar and hydrochar production and applications: a review. Energy 2019;171:581–98. https://doi.org/10.1016/j.energy.2019.01.035.

[20] Chu G, Zhao J, Huang Yu, Zhou D, Liu Y, Wu M, et al. Phosphoric acid pretreatment enhances the specific surface areas of biochars by generation of micropores. Environ Pollut 2018;240:1–9. https://doi.org/10.1016/j.envpol.2018.04.003.

[21] Yuan Y, Yuan T, Wang D, Tang J, Zhou S. Sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in an microbial fuel cell. Bioresour Technol 2013;144:115–20. https://doi.org/10.1016/j.biortech.2013.06.075.
[22] Huggins T, Wang H, Kearns J, Jenkins P, Ren ZJ. Biochar as a sustainable electrode material for electricity production in microbial fuel cells. Bioresour Technol 2014;157:114–9. https://doi.org/10.1016/j.biortech.2014.01.058.
[23] Huggins TM, Pietron JJ, Wang H, Ren ZJ, Biffinger JC. Graphitic biochar as a cathode electrocatalyst support for microbial fuel cells. Bioresour Technol 2015; 195:147–53. https://doi.org/10.1016/j.biortech.2015.06.012.
[24] Wang B, Wang Z, Jiang Y, Tan G, Xu N, Xu Y. Enhanced power generation and wastewater treatment in sustainable biochar electrodes based bioelectrochemical system. Bioresour Technol 2017;241:841–8. https://doi.org/10.1016/j.biortech.2017.05.155.
[25] Li M, Zhang H, Xiao T, Wang S, Zhang B, Chen D, et al. Low-cost biochar derived from corncob as oxygen reduction catalyst in air cathode microbial fuel cells. Electrochim Acta 2018;283:780–8. https://doi.org/10.1016/j.electacta.2018.07.010.
[26] Zhong K, Li M, Yang Y, Zhang H, Zhang B, Tang J, et al. Nitrogen-doped biochar derived from watermelon rind as oxygen reduction catalyst in air cathode microbial fuel cells. Appl Energy 2019;242:516–25. https://doi.org/10.1016/j.apenergy.2019.03.050.
[27] Marzorati S, Goglio A, Fest-Santini S, Mombelli D, Villa F, Cristiani P, et al. Air-breathing bio-cathodes based on electro-active biochar from pyrolysis of giant cane stalks. Int J Hydrog Energy 2019;44(9):4496–507. https://doi.org/10.1016/j.ijhydene.2018.07.167.
[28] Chaijak P, Sato C, Lertworapreecha M, Sukkasem C, Boonsawang P, Paucar N. Potential of biochar-anode in a ceramic-separator microbial fuel cell (CMFC) with a Laccase-based air cathode. Pol J Environ Stud 2020;29(1):499–503. https://doi.org/10.15244/pjoes/99099.
[29] Xiao R, Awasthi MK, Li R, Park J, Pensky SM, Wang Q, et al. Recent developments in biochar utilization as an additive in organic solid waste composting: a review. Bioresour Technol 2017;246:203–13. https://doi.org/10.1016/j.biortech.2017.07.090.
[30] Yu KL, Lau BF, Show PL, Ong HC, Ling TC, Chen W-H, et al. Recent developments on algal biochar production and characterization. Bioresour Technol 2017;246:2–11. https://doi.org/10.1016/j.biortech.2017.08.009.
[31] Guizani C, Valin S, Billaud J, Peyrot M, Salvador S. Biomass fast pyrolysis in a drop tube reactor for bio oil production: experiments and modeling. Fuel 2017; 207:71–84. https://doi.org/10.1016/j.fuel.2017.06.068.
[32] Fang J, Zhan L, Ok YS, Gao B. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J Ind Eng Chem 2018;57:15–21. https://doi.org/10.1016/j.jiec.2017.08.026.
[33] Uchimiya M, Hiradate S, Antal MJ. Influence of carbonization methods on the aromaticity of pyrogenic dissolved organic carbon. Energy Fuels 2015;29(4):2503–13. https://doi.org/10.1021/acs.energyfuels.5b00146.
[34] Chen W-H, Peng J, Bi XT. A state-of-the-art review of biomass torrefaction, densification and applications. Renew Sustain Energy Rev 2015;44:847–66. https://doi.org/10.1016/j.rser.2014.12.039.
[35] Tripathi M, Sahu JN, Ganesan P. Effect of process parameters on production of biochar from biomass waste through pyrolysis: a review. Renew Sustain Energy Rev 2016;55:467–81. https://doi.org/10.1016/j.rser.2015.10.122.
[36] Weber K, Quicker P. Properties of biochar. Fuel 2018;217:240–61. https://doi.org/10.1016/j.fuel.2017.12.054.
[37] González T, Ureta-Zañartu MS, Marco JF, Vidal G. Effect of Zeolite-Fe on graphite anode in electroactive biofilm development for application in microbial fuel cells. Appl Surf Sci 2019;467–468:851–9. https://doi.org/10.1016/j.apsusc.2018.10.120.
[38] Cai T, Meng L, Chen G, Xi Yu, Jiang N, Song J, et al. Application of advanced anodes in microbial fuel cells for power generation: a review. Chemosphere 2020; 248:125985. https://doi.org/10.1016/j.chemosphere.2020.125985.
[39] Xin S, Shen J, Liu G, Chen Q, Xiao Z, Zhang G, et al. High electricity generation and COD removal from cattle wastewater in microbial fuel cells with 3D air cathode employed non-precious Cu2O/reduced graphene oxide as cathode catalyst. Energy 2020;196:117123. https://doi.org/10.1016/j.energy.2020.117123.
[40] Ye Y, Duan W, Yi X, Lei Z, Li Ge, Feng C. Biogenic precursor to size-controlled synthesis of Fe2P nanoparticles in heteroatom-doped graphene-like carbons and their electrocatalytic reduction of oxygen. J Power Sources 2019;435:226770. https://doi.org/10.1016/j.jpowsour.2019.226770.
[41] Noori MT, Bhowmick GD, Tiwari BR, Ghangrekar OM, Ghangrekar MM, Mukherjee CK. Carbon supported Cu-Sn bimetallic alloy as an excellent low-cost cathode catalyst for enhancing oxygen reduction reaction in microbial fuel cell. J Electrochem Soc 2018;165(9):F621–8. https://doi.org/10.1149/2.0271809jes.
[42] Sunyoto NMS, Zhu M, Zhang Z, Zhang D. Effect of biochar addition on hydrogen and methane production in two-phase anaerobic digestion of aqueous carbohydrates food waste. Bioresour Technol 2016;219:29–36. https://doi.org/10.1016/j.biortech.2016.07.089.
[43] Qin Y, Yin X, Xu X, Yan X, Bi F, Wu W. Specific surface area and electron donating capacity determine biochar's role in methane production during anaerobic digestion. Bioresour Technol 2020;303:122919. https://doi.org/10.1016/j.biortech.2020.122919.
[44] Farkas É, Feigl V, Gruiz K, Vaszita E, Fekete-Kertész I, Tolner M, et al. Long-term effects of grain husk and paper fibre sludge biochar on acidic and calcareous sandy soils – a scale-up field experiment applying a complex monitoring toolkit. Sci Total Environ 2020;731:138988. https://doi.org/10.1016/j.scitotenv.2020.138988.
[45] Yue Y, Shen C, Ge Y. Biochar accelerates the removal of tetracyclines and their intermediates by altering soil properties. J Hazard Mater 2019;380:120821. https://doi.org/10.1016/j.jhazmat.2019.120821.
[46] Claoston N, Samsuri AW, Ahmad Husni MH, Mohd Amran MS. Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. Waste Manag Res 2014;32(4):331–9. https://doi.org/10.1177/0734242X14525822.
[47] Rehrah D, Reddy MR, Novak JM, Bansode RR, Schimmel KA, Yu J, et al. Production and characterization of biochars from agricultural by-products for use in soil quality enhancement. J Anal Appl Pyrol 2014;108:301–9. https://doi.org/10.1016/j.jaap.2014.03.008.
[48] Liang B, Li K, Liu Y, Kang X. Nitrogen and phosphorus dual-doped carbon derived from chitosan: an excellent cathode catalyst in microbial fuel cell. Chem Eng J 2019;358:1002–11. https://doi.org/10.1016/j.cej.2018.09.217.
[49] Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, et al. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 2014;99:19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071.
[50] Dehkhoda AM, West AH, Ellis N. Biochar based solid acid catalyst for biodiesel production. Appl Catal Gen 2010;382(2):197–204. https://doi.org/10.1016/j.apcata.2010.04.051.
[51] Dehkhoda AM, Ellis N. Biochar-based catalyst for simultaneous reactions of esterification and transesterification. Catal Today 2013;207:86–92. https://doi.org/10.1016/j.cattod.2012.05.034.
[52] Li S, Gu Z, Bjornson BE, Muthukumarappan A. Biochar based solid acid catalyst hydrolyze biomass. J Environ Chem Eng 2013;1(4):1174–81. https://doi.org/10.1016/j.jece:2013.09.004.
[53] Cha JS, Choi J-C, Ko JH, Park Y-K, Park SH, Jeong K-E, et al. The low-temperature SCR of NO over rice straw and sewage sludge derived char. Chem Eng J 2010;156(2):321–7. https://doi.org/10.1016/j.cej.2009.10.027.
[54] Kastner JR, Miller J, Geller DP, Locklin J, Keith LH, Johnson T. Catalytic esterification of fatty acids using solid acid catalysts generated from biochar and activated carbon. Catal Today 2012;190(1):122–32. https://doi.org/10.1016/j.cattod.2012.02.006.
[55] Manyà JJ. Pyrolysis for biochar purposes: a review to establish current knowledge gaps and research needs. Environ Sci Technol 2012;46(15):7939–54. https://doi.org/10.1021/es301029g.
[56] Liao C, Wu C, Yan Y. The characteristics of inorganic elements in ashes from a 1 MW CFB biomass gasification power generation plant. Fuel Process Technol 2007; 88(2):149–56. https://doi.org/10.1016/j.fuproc.2005.06.008.
[57] Brewer CE, Schmidt-Rohr K, Satrio JA, Brown RC. Characterization of biochar from fast pyrolysis and gasification systems. Environ Prog Sustain Energy 2009; 28(3):386–96. https://doi.org/10.1002/ep.v28:310.1002/ep.10378.
[58] Spokas KA, Novak JM, Masiello CA, Johnson MG, Colosky EC, Ippolito JA, et al. Physical disintegration of biochar: an overlooked process. Environ Sci Technol Lett 2014;1(8):326–32. https://doi.org/10.1021/ez500199t.
[59] Sharma RK, Wooten JB, Baliga VL, Lin X, Geoffrey Chan W, Hajaligol MR. Characterization of chars from pyrolysis of lignin. Fuel 2004;83(11-12):1469–82. https://doi.org/10.1016/j.fuel.2003.11.015.
[60] Mukome FND, Zhang X, Silva LCR, Six J, Parikh SJ. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. J Agric Food Chem 2013;61(9):2196–204. https://doi.org/10.1021/jf3049142.
[61] Qian L, Chen B. Interactions of aluminum with biochars and oxidized biochars: implications for the biochar aging process. J Agric Food Chem 2014;62(2):373–80. https://doi.org/10.1021/jf404624h.
[62] Liu W-J, Zeng F-X, Jiang H, Zhang X-S. Preparation of high adsorption capacity bio-chars from waste biomass. Bioresour Technol 2011;102(17):8247–52. https://doi.org/10.1016/j.biortech.2011.06.014.
[63] Li Y, Shao J, Wang X, Deng Y, Yang H, Chen H. Characterization of modified biochars derived from bamboo pyrolysis and their utilization for target component (furfural) adsorption. Energy Fuels 2014;28(8):5119–27. https://doi.org/10.1021/ef500725c.
[64] Zhong Y, Deng Q, Zhang P, Wang J, Wang R, Zeng Z, et al. Sulfonic acid functionalized hydrophobic mesoporous biochar: design, preparation and acid-catalytic properties. Fuel 2019;240:270–7. https://doi.org/10.1016/j.fuel.2018.11.152.
[65] Xiu S, Shahbazi A, Li R. Characterization, modification and application of biochar for energy storage and catalysis: a review. Trends Renewable Energy 2017;3(1):86–101. https://doi.org/10.17737/tre.2017.3.1.0033.
[66] Cheng F, Li X. Preparation and application of biochar-based catalysts for biofuel production. Catalysts 2018;8(9):346. https://doi.org/10.3390/catal8090346.
[67] Luo Y, Street J, Steele P, Entsminger E, Guda V. Activated carbon derived from pyrolyzed pinewood char using elevated temperature, KOH, H3PO4, and H2O2. BioResources 2016;11(4):10433–47.
[68] Frank B, Zhang J, Blume R, Schlögl R, Su D. Heteroatoms increase the selectivity in oxidative dehydrogenation reactions on nanocarbons. Angew Chem Int Ed 2009;48(37):6913–7. https://doi.org/10.1002/anie.200901826.
[69] Gong K, Du F, Xia Z, Durstock M, Dai L. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. Science 2009;323(5915):760–4. https://doi.org/10.1126/science:1168049.
[70] Hao L, Yu J, Xu X, Yang L, Xing Z, Dai Y, et al. Nitrogen-doped MoS2/carbon as highly oxygen-permeable and stable catalysts for oxygen reduction reaction in microbial fuel cells. J Power Sources 2017;339:68–79. https://doi.org/10.1016/j.jpowsour.2016.11.041.
[71] Nguyen M-V, Lee B-K. A novel removal of CO2 using nitrogen doped biochar beads as a green adsorbent. Process Saf Environ Prot 2016;104:490–8. https://doi.org/10.1016/j.psep.2016.04.007.

[72] Suhas, Carrott PJM, Ribeiro Carrott MML. Lignin – from natural adsorbent to activated carbon: a review. Bioresour Technol 2007;98(12):2301–12. https://doi.org/10.1016/j.biortech.2006.08.008.
[73] Liu Q, Zhou Y, Chen S, Wang Z, Hou H, Zhao F. Cellulose-derived nitrogen and phosphorus dual-doped carbon as high performance oxygen reduction catalyst in microbial fuel cell. J Power Sources 2015;273:1189–93. https://doi.org/10.1016/j.jpowsour.2014.09.102.
[74] Leng Y, Liu J, Jiang P, Wang J. POSS-derived mesostructured amphiphilic polyoxometalate-based ionic hybrids as highly efficient epoxidation catalysts. ACS Sustain Chem Eng 2015;3(1):170–6. https://doi.org/10.1021/sc500674q.
[75] Huang J, Feng H, Jia Y, Shen D, Xu Y. Sewage sludge-derived carbon-doped manganese as efficient cathode catalysts in microbial fuel cells. Water Sci Technol 2019;80:1399–406. https://doi.org/10.2166/wst.2019.344.
[76] Chen W, Liu Z, Li Y, Jiang K, Hou J, Lou X, et al. A novel stainless steel fiber felt/Pd nanocatalysts electrode for efficient ORR in air-cathode microbial fuel cells. Electrochim Acta 2019;324:134862. https://doi.org/10.1016/j.electacta.2019.134862.
[77] Tajdid Khajeh R, Aber S, Nofouzi K. Efficient improvement of microbial fuel cell performance by the modification of graphite cathode via electrophoretic deposition of CuO/ZnO. Mater Chem Phys 2020;240:122208. https://doi.org/10.1016/j.matchemphys.2019.122208.
[78] Huggins TM, Latorre A, Biffinger JC, Ren Z. Biochar based microbial fuel cell for enhanced wastewater treatment and nutrient recovery. Sustainability 2016;8(2):169. https://doi.org/10.3390/su8020169.
[79] You K, Zhou Z, Gao C, Yang Q. One-step preparation of biochar electrodes and their applications in sediment microbial electrochemical systems. Catalysts 2021;11:508. https://doi.org/10.3390/catal11040508.
[80] Zhang F, Cheng S, Pant D, Bogaert GV, Logan BE. Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell. Electrochem Commun 2009;11(11):2177–9. https://doi.org/10.1016/j.elecom.2009.09.024.
[81] Huggins TM, Haeger A, Biffinger JC, Ren ZJ. Granular biochar compared with activated carbon for wastewater treatment and resource recovery. Water Res 2016;94:225–32. https://doi.org/10.1016/j.watres.2016.02.059.
[82] Qian K, Kumar A, Zhang H, Bellmer D, Huhnke R. Recent advances in utilization of biochar. Renew Sustain Energy Rev 2015;42:1055–64. https://doi.org/10.1016/j.rser.2014.10.074.
[83] Li S, Ho SH, Hua T, Zhou Q, Li F, Tang J. Sustainable biochar as electrocatalysts for the oxygen reduction reaction in microbial fuel cells. Green Energy Environ 2020. https://doi.org/10.1016/j.gee.2020.11.010.
[84] Yesilyurt MK, Arslan M, Eryilmaz T. Application of response surface methodology for the optimization of biodiesel production from yellow mustard (Sinapis Alba L.) seed oil. Int J Green Energy 2019;16(1):60–71. https://doi.org/10.1080/15435075.2018.1532431.
[85] Md Khudzari J, Gariépy Y, Kurian J, Tartakovsky B, Raghavan GSV. Effects of biochar anodes in rice plant microbial fuel cells on the production of bioelectricity, biomass, and methane. Biochem Eng J 2019;141:190–9. https://doi.org/10.1016/j.bej.2018.10.012.
[86] Senthilkumar N, Pannipara M, Al-Sehemi AG, Gnana kumar G. PEDOT/NiFe2O4 nanocomposites on biochar as a free-standing anode for high-performance and durable microbial fuel cells. New J Chem 2019;43(20):7743–50. https://doi.org/10.1039/C9NJ00638A.
[87] Ganesh K, Jambeck JR. Treatment of landfill leachate using microbial fuel cells: alternative anodes and semi-continuous operation. Bioresour Technol 2013;139:383–7. https://doi.org/10.1016/j.biortech.2013.04.013.
[88] Yaqoob AA, Ibrahim MNM, Guerrero-Barajas C. Modern trend of anodes in microbial fuel cells (MFCs): an overview. Environ Technol Innov 2021;23:101579. https://doi.org/10.1016/j.eti.2021.101579.
[89] Sawant SY, Han TH, Cho MH. Metal-free carbon-based materials: promising electrocatalysts for oxygen reduction reaction in microbial fuel cells. Int J Mol Sci 2017;18(1):25. https://doi.org/10.3390/ijms18010025.
[90] Ma L-L, Liu W-J, Hu X, Lam PKS, Zeng JR, Yu H-Q. Ionothermal carbonization of biomass to construct sp2/sp3 carbon interface in N-doped biochar as efficient oxygen reduction electrocatalysts. Chem Eng J 2020;400:125969. https://doi.org/10.1016/j.cej.2020.125969.
[91] Lee J, Sarmah AK, Kwon EE. Production and formation of biochar. In: Biochar from Biomass and Waste. Elsevier; 2019. p. 3–18. https://doi.org/10.1016/B978-0-12-811729-3.00001-7.
[92] Yuan Y, Liu T, Fu P, Tang J, Zhou S. Conversion of sewage sludge into high-performance bifunctional electrode materials for microbial energy harvesting. J Mater Chem A 2015;3(16):8475–82. https://doi.org/10.1039/C5TA00458F.
[93] Yuan H, Deng L, Qi Y, Kobayashi N, Tang J. Nonactivated and activated biochar derived from bananas as alternative cathode catalyst in microbial fuel cells. Sci World J 2014;2014:1–8. https://doi.org/10.1155/2014/832850.
[94] Guo Z, Xie C, Zhang P, Zhang J, Wang G, He X, et al. Toxicity and transformation of graphene oxide and reduced graphene oxide in bacteria biofilm. Sci Total Environ 2017;580:1300–8. https://doi.org/10.1016/j.scitotenv.2016.12.093.
[95] Mo R-J, Zhao Y, Wu M, Xiao H-M, Kuga S, Huang Y, et al. Activated carbon from nitrogen rich watermelon rind for high-performance supercapacitors. RSC Adv 2016;6(64):59333–42. https://doi.org/10.1039/C6RA10719B.
[96] Jiang H, Zhu Y, Feng Q, Su Y, Yang X, Li C. Nitrogen and phosphorus dual-doped hierarchical porous carbon foams as efficient metal-free electrocatalysts for oxygen reduction reactions. Chem – Eur J 2014;20(11):3106–12. https://doi.org/10.1002/chem.201304561.
[97] Dong J, Wu Y, Wang C, Lu H, Li Y. Three-dimensional electrodes enhance electricity generation and nitrogen removal of microbial fuel cells. Bioprocess Biosyst Eng 2020;43(12):2165–74. https://doi.org/10.1007/s00449-020-02402-9.
[98] Senthilkumar K, Naveenkumar M. Enhanced performance study of microbial fuel cell using waste biomass-derived carbon electrode. Biomass Convers Biorefinery 2021. https://doi.org/10.1007/s13399-021-01505-x.
[99] Das I, Das S, Dixit R, Ghangrekar MM. Goethite supplemented natural clay ceramic as an alternative proton exchange membrane and its application in microbial fuel cell. Ionics 2020;26(6):3061–72. https://doi.org/10.1007/s11581-020-03472-1.
[100] Neethu B, Bhowmick GD, Ghangrekar MM. A novel proton exchange membrane developed from clay and activated carbon derived from coconut shell for application in microbial fuel cell. Biochem Eng J 2019;148:170–7. https://doi.org/10.1016/j.bej.2019.05.011.
[101] Salarizadeh P, Javanbakht M, Pourmahdian S, Hazer MSA, Hooshyari K, Askari MB. Novel proton exchange membranes based on proton conductive sulfonated PAMPS/PSSA-TiO2 hybrid nanoparticles and sulfonated poly (Ether Ether Ketone) for PEMFC. Int J Hydrog Energy 2019;44(5):3099–114. https://doi.org/10.1016/j.ijhydene.2018.11.235.
[102] Allam F, Elnouby M, El-Khatib KM, El-Badan DE, Sabry SA. Water hyacinth (Eichhornia Crassipes) biochar as an alternative cathode electrocatalyst in an air-cathode single chamber microbial fuel cell. Int J Hydrog Energy 2020;45(10):5911–27. https://doi.org/10.1016/j.ijhydene.2019.09.164.
[103] Pepè Sciarria T, de Oliveira MAC, Mecheri B, D'Epifanio A, Goldfarb JL, Adani F. Metal-free activated biochar as an oxygen reduction reaction catalyst in single chamber microbial fuel cells. J Power Sources 2020;462:228183. https://doi.org/10.1016/j.jpowsour.2020.228183.
[104] Chakraborty I, Das S, Dubey BK, Ghangrekar MM. Novel low cost proton exchange membrane made from sulphonated biochar for application in microbial fuel cells. Mater Chem Phys 2020;239:122025. https://doi.org/10.1016/j.matchemphys.2019.122025.
[105] Deng L, Yuan H, Cai X, Ruan Y, Zhou S, Chen Y, et al. Honeycomb-like hierarchical carbon derived from livestock sewage sludge as oxygen reduction reaction catalysts in microbial fuel cells. Int J Hydrog Energy 2016;41(47):22328–36. https://doi.org/10.1016/j.ijhydene.2016.08.132.
[106] Zhou L, Fu P, Wen D, Yuan Y, Zhou S. Self-constructed carbon nanoparticles-coated porous biocarbon from plant moss as advanced oxygen reduction catalysts. Appl. Catal. B Environ. 2016;181:635–43. https://doi.org/10.1016/j.apcatb.2015.08.035.
[107] Yuan H, Deng L, Cai X, Zheng T, Zhou S, Chen Y, et al. Recycling electroplating sludge to produce sustainable electrocatalysts for the efficient conversion of carbon dioxide in a microbial electrolysis cell. Electrochim Acta 2016;222:177–84. https://doi.org/10.1016/j.electacta.2016.10.180.
[108] Yuan H, He Z. Platinum group metal–free catalysts for hydrogen evolution reaction in microbial electrolysis cells. Chem Rec 2017;17(7):641–52. https://doi.org/10.1002/tcr.v17.710.1002/tcr.201700007.
[109] Hossen M, Artyushkova K, Atanassov P, Serov A. Synthesis and characterization of high performing Fe-NC catalyst for oxygen reduction reaction (ORR) in Alkaline Exchange Membrane Fuel Cells. J Power Sources 2018;375:214–21. https://doi.org/10.1016/j.jpowsour.2017.08.036.
[110] Liu X, Yu Y, Niu Y, Bao S, Hu W. Cobalt nanoparticle decorated graphene aerogel for efficient oxygen reduction reaction electrocatalysis. Int J Hydrog Energy 2017;42(9):5930–7. https://doi.org/10.1016/j.ijhydene.2017.02.009.
[111] Jiang B, Muddemann T, Kunz U, Bormann H, Niedermeiser M, Haupt D, et al. Evaluation of microbial fuel cells with graphite plus MnO_2 and MoS_2 paints as oxygen reduction cathode catalyst. J Electrochem Soc 2017;164(3):H3083–90. https://doi.org/10.1149/2.0131703jes.
[112] Homagain K, Shahi C, Luckai N, Sharma M. Life cycle cost and economic assessment of biochar-based bioenergy production and biochar land application in Northwestern Ontario, Canada. For. Ecosyst. 2016;3:1–10. https://doi.org/10.1186/s40663-016-0081-8.